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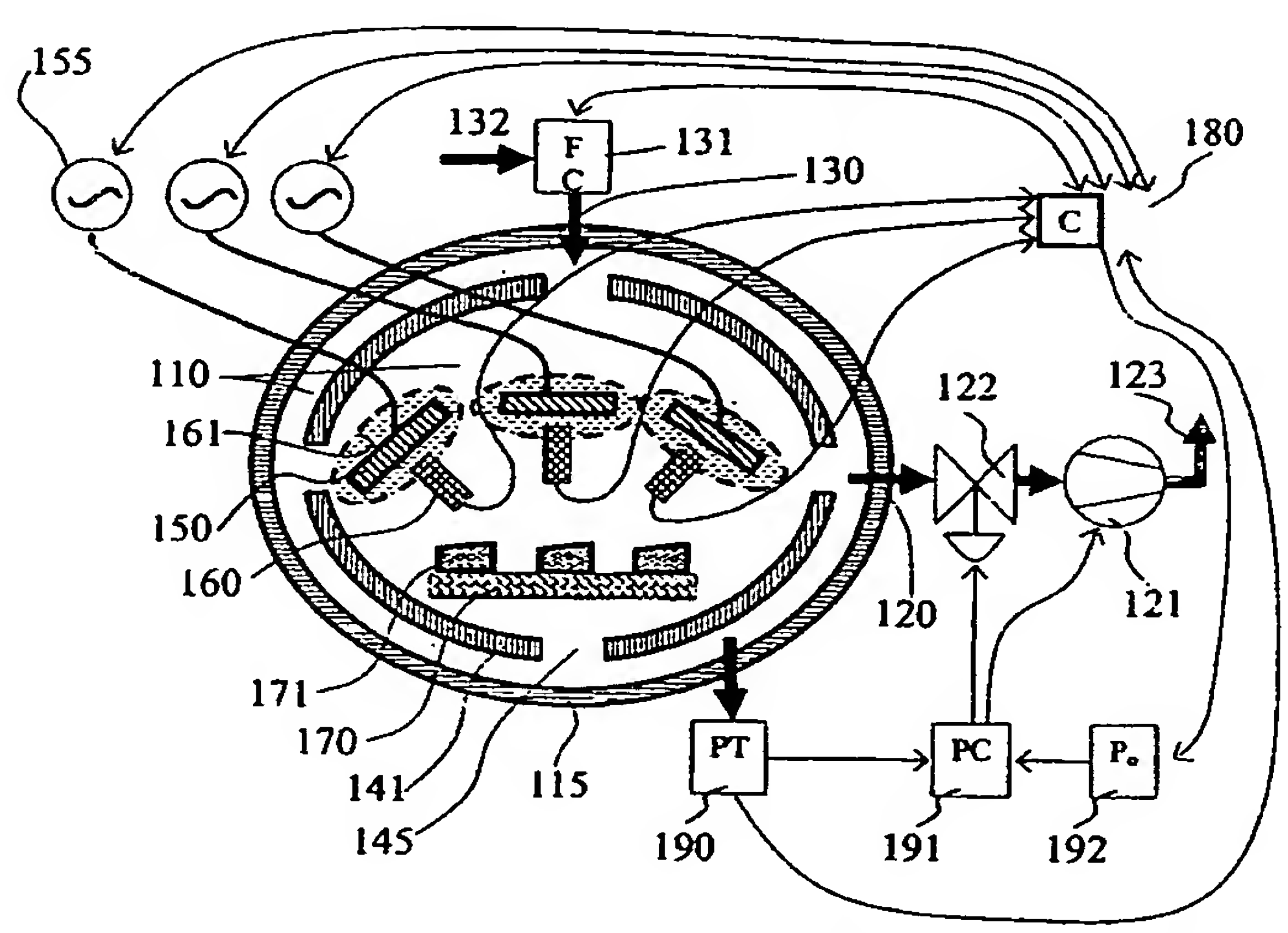
(54) Title: METHOD AND APPARATUS FOR GAS PLASMA TREATMENT WITH CONTROLLED EXTENT OF GAS PLASMA, AND USE THEREOF



(57) Abstract: A method of controlling the extent of gas plasma, the method comprising: (A) providing a gas zone (110), said gas zone comprising a gas having a pressure; said gas comprising at least one gas component allowing generation of a plasma; (B) generating a plasma in said gas zone by supplying a potential difference between at least two electrodes (150); said at least two electrodes being configured to wholly or partly encompass said gas zone; and (C) controlling the extent of said generated plasma by controlling at least one of: said gas, said pressure, said potential difference, and said configuration of said at least two electrodes; a plasma treatment apparatus comprising at least one plasma measuring means (160) for measuring the extent of the plasma, and at least one controlling means (180, 191, 131) for controlling the extent of the plasma; and use of the method and apparatus in plasma treatment and/or plasma-assisted surface modification of electrodes and/or substrates.

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METHOD AND APPARATUS FOR GAS PLASMA TREATMENT WITH CONTROLLED EXTENT OF GAS PLASMA, AND USE THEREOF

DESCRIPTION

1. BACKGROUND OF THE INVENTION

The present invention relates to a method of controlling the extent of gas plasma, a plasma treatment apparatus with controlled extent of gas plasma, and use thereof in plasma treatments and plasma-assisted surface modification of electrodes and substrates, preferably including plasma cleaning, plasma etching, plasma activation, and plasma deposition of electrodes, substrates, or both.

The Technical Field

Generally, in a plasma treatment apparatus comprising plasma generating electrodes and optionally other objects arranged within the generated plasma, contamination of the plasma generating electrodes increases the electrode resistance over the electrode-gas interface. Such an increased electrode resistance affects the plasma generation conditions e.g. by lowering the average plasma power density at constant voltage supplied to the electrodes. Some effects of increased electrode resistance can be remedied by increasing the voltage supplied to the electrodes. However, at high voltages, the risk of spark generation is increased thereby reducing the reliability of the apparatus.

Also, contaminated plasma generating electrodes and optionally other contaminated objects contaminate the

treatment plasma gas, e.g. a deposition gas or an etching gas for a subsequent plasma treatment.

Electrode contamination can be reduced by including an electrode-cleaning step, e.g. a manual or an automatic cleaning treatment of the electrodes, before each substrate treatment process. However, generally electrode cleaning requires the apparatus to be shut down during the cleaning process, which is both time consuming and reduces production efficiency.

Further, for electrode cleaning comprising plasma cleaning of the electrodes by a plasma cleaning gas, the plasma cleaning of electrodes may negatively affect other objects present in the plasma apparatus, e.g. sensors, such as deposition monitoring sensors, plasma intensity sensors, sputtering electrodes, substrate holders, and substrates of which some are desired to be cleaned while others are not.

Therefore, there is a need for a method and apparatus for plasma treatment which allow for plasma electrode cleaning without negatively affecting surfaces of components and substrates inside the plasma apparatus.

Prior Art Disclosures

Methods and apparatus for sub-radio frequency gas plasma deposition are disclosed in EP 0 741 404, WO 00/44 207, and WO 02/35 895, however, none of these prior arts relates to control of extent of plasma for improving plasma treatment, in particular plasma treatment productivity

US patent No. 6 379 575 discloses an apparatus and process for treating and conditioning an etching chamber, including cleaning etch residues on the walls and components thereof, the cleaning step comprising providing an activated cleaning gas by applying micro wave or RF energy and introducing the activated cleaning gas at a high flow rate into the etching chamber.

US 5 817 534 discloses a RF plasma reactor with a capacitive cleaning electrode for cleaning during processing of semiconductor wafers.

US 5 514 246 discloses a plasma reactor and a method of cleaning away material adhering to its internal walls, the method comprising injecting a cleaning gas into the reactor, said cleaning gas being activated between a pair of capacitive-coupled conductors at least one of which is externally of the reactor, and drawn in the direction of the external electrode impacting and cleaning away the adhered material.

2. DISCLOSURE OF THE INVENTION

Object of the invention

In an aspect, it is an object of the present invention to seek to provide an improved method and apparatus for plasma treatment of objects.

In particular such a method and apparatus exhibiting improved productivity.

It is a further object of the present invention to seek to provide such a method and apparatus wherein, during

plasma electrode cleaning, objects to be plasma treated can be present in the plasma apparatus.

Further objects appear from the description elsewhere.

Solution According to the Invention

"Method of controlling the extent of plasma"

Even though there have been a need for cleaning plasma generating electrodes placed in a plasma generating reactor during plasma treatment of a substrate in a simple and fast way, it has not until now been suggested to clean such electrodes with the substrate is within the plasma generating reactor during the cleaning thereof.

The invention in this aspect thus provides a very effective and simple method of plasma treating a substrate and cleaning the electrodes before and/or after the plasma treatment of the substrate.

Thus it has not until now been considered possible to clean an electrode with a substrate within the plasma generating reactor without damaging the substrate.

The plasma generating reactor being defined as the space within which gas can move without hindrance when the plasma is turned of (e.g. immediately prior to turning on the plasma) and which includes the plasma zone when the plasma in turned on.

In an aspect, according to the present invention, these objects are fulfilled by providing a method of controlling the extent of gas plasma, the method comprising:

(A) providing a gas zone, said gas zone comprising a gas having a pressure; said gas comprising at least one gas component allowing generation of a plasma;

(B) generating a plasma in said gas zone by supplying a potential difference between at least two electrodes; said at least two electrodes being configured to wholly or partly encompass said gas zone; and

(C) controlling the extent of said generated plasma by controlling at least one of: said gas, said pressure, said potential difference, and said configuration of said at least two electrodes;

whereby the distribution of plasma and the exposure to plasma of objects or parts of objects in a plasma treating apparatus can be controlled.

This control of extent of plasma can be used to improved productivity of plasma treatment methods, including plasma treatments such as plasma etching, plasma deposition, and plasma metallization of substrates, as well as plasma cleaning of electrodes and other objects of the apparatus, including plasma sensors, and deposition sensors.

For example, a controlled plasma distribution allows exposure of electrodes without exposing other objects to the plasma, e.g. a substrate or a part thereof, whereby electrodes can be cleaned by plasma cleaning in presence of substrates and a separate process step for electrode

plasma cleaning can be avoided. This saves time otherwise used to shut down the apparatus and to evacuate the apparatus once the electrode has been cleaned and the new substrate has been introduced in to the apparatus. Consequently, the number of plasma treated substrates per unit time can be increased.

Further, a controlled plasma distribution allows exposure of selected objects or parts thereof whereby contamination thereof by plasma deposits can be reduced or avoided.

Thus the invention in particular relates to a method of plasma treating a substrate further comprising the step of cleaning one or more plasma generating electrodes while the substrate and one or more plasma generating electrodes is present in the same reaction chamber, the method includes the step of adjusting the plasma zone so that the substrate is within the plasma zone during the plasma treatment thereof, and is out of the plasma zone during the cleaning of the one or more plasma generating electrodes.

In one embodiment the method of plasma treating a substrate comprising the step of cleaning one or more plasma generating electrodes while the substrate and one or more plasma generating electrodes is present in the same reaction chamber, the method includes the step of moving the one or more electrodes preferably within the reaction chamber so that the substrate is within the plasma zone during the plasma treatment thereof, and is out of the plasma zone during the cleaning of the one or more plasma generating electrodes.

In one embodiment the method of plasma treating a substrate comprising the step of cleaning one or more plasma generating electrodes while the substrate and one or more plasma generating electrodes is present in the same reaction chamber, the method includes the step of changing the pressure within the reaction chamber so that the object to be plasma treated is within the plasma zone during the plasma treatment thereof, and is out of the plasma zone during the cleaning of the one or more plasma generating electrodes.

In one embodiment the method of plasma treating an object comprising the step of cleaning one or more plasma generating electrodes while the object to be plasma treated and one or more plasma generating electrodes is present in the same reaction chamber, the method includes the step of changing the potential difference between the one or more electrodes so that the object to be plasma treated is within the plasma zone during the plasma treatment thereof, and is out of the plasma zone during the cleaning of the one or more plasma generating electrodes.

In one embodiment the method of plasma treating an object comprising the step of cleaning one or more plasma generating electrodes while the object to be plasma treated and one or more plasma generating electrodes is present in the same reaction chamber, the method includes the step of inserting or moving a shield or mask so that the object to be plasma treated is within the plasma zone during the plasma treatment thereof, and is out of the plasma zone during the cleaning of the one or more plasma generating electrodes.

In one embodiment the method of plasma treating an object comprising the step of cleaning one or more plasma generating electrodes while the object to be plasma treated and one or more plasma generating electrodes is present in the same reaction chamber, the method includes the step of applying and/or moving an electric or magnetic field in the reactor chamber so that the object to be plasma treated is within the plasma zone during the plasma treatment thereof, and is out of the plasma zone during the cleaning of the one or more plasma generating electrodes.

The invention also relates to a method of plasma treating an object further comprising the step of cleaning one or more plasma generating electrodes while the object to be plasma treated and one or more plasma generating electrodes is present in the same reaction chamber, the method includes the step of moving the object to be plasma treated within the reaction chamber so that the object to be plasma treated is within the plasma zone during the plasma treatment thereof, and is out of the plasma zone during the cleaning of the one or more plasma generating electrodes.

"Type of gas, composition, and amounts"

Generally, the gas of the gas zone comprises any suitable gas comprising at least one gas component allowing generation of plasma.

The generation of plasma and thus implicitly the extent thereof depends on the type of gas used for generating the plasma. Further, when the gas consists of more gases,

the composition and amounts of these components influence the generation of plasma as well.

In a preferred embodiment, the extent of said generated plasma is controlled by controlling the type of said gas, its composition, and/or the amount of its components whereby the extent of plasma can be controlled by selecting a gas having the ability to generate plasma.

Generally, different abilities to generate plasma result in different extents of plasma. A mixture of Ar and N_2O for etching application provides an extent of plasma that differs from the extent of plasma of a mixture of He and a monomer for plasma polymerisation deposition. If a constant extent of plasma is desired, the modified extent of plasma can be compensated by applying other means of said means for controlling the extent of plasma, e.g. the pressure or the applied potential difference.

The type, composition, and amounts of gas can be controlled by admitting a different type of gas into the gas zone, and/or letting a gas component out of the gas zone, e.g. replacing an oxidizing/reducing cleaning gas for plasma cleaning with a monomer deposition gas for plasma deposition.

In a preferred embodiment, said gas zone contains a gas component, or a gas composition, selected from the group comprising:

inert gasses, including noble gasses, preferably He, Ar, Ne, Xe;

oxidizing gasses, preferably O_2, NO_2, N_2O, CO_2;

halogen gasses, preferably Cl_2, F_2;

and reducing gasses, preferably H_2 and NH_3;

mixtures of said noble gasses with said halogen gasses, said oxidizing gasses, or with said reducing gasses;

a mixture of said halogen gasses with said oxidizing gasses, or with said reducing gasses; and

plasma polymerisable substances, including monomers, preferably selected from the group consisting of aliphatic hydrocarbons, including C_1-C_{16} alkanes such ethane, hexane; C_2-C_{16} alkenes such as hexene, 1-hexene, 3-methyl-1-hexene, dienes such as 1,4-hexadiene, butadiene), 1,4-hexadiene; C_2-C_{16} alkynes including hexyne, 1-hexyne; aromatic hydrocarbons, including styrene, benzene; substituted benzenes; aromatic monomers of styrene compounds; monomers of vinyl compounds, including vinylpyrrolidone; acrylate compounds including methylacrylate, acrylonitrile, glycidylmethacrylate, methacrylacid-anhydride, and acrylic acid chloride,

and mixtures of said polymerisable substances and said inert gasses, halogen gasses, oxidizing gasses and reducing gasses;

whereby treatments for e.g. etching and cleaning with inert gases, oxidizing, reducing gasses, or mixtures thereof can be obtained; and further, plasma polymerisation with substances that can be plasma-polymerized can be obtained under conditions of a controlled extent of plasma.

Other useful gasses that should be mentioned include cyanoacrylic and acetylene which may be used alone, in combination as well as in combinations with the above mentioned gasses.

"Gas pressure"

Generally, the pressure conditions of the gas include vacuum. A too low pressure does not provide enough gas for plasma to be generated, and a too high pressure quenches generated plasma.

The pressure can be controlled by selection of gas outlet and gas inlet by means of pumps and valves, and associated control equipment known to a skilled person in the art. More details are disclosed together with the description of the apparatus.

In a preferred embodiment, said pressure is controlled by controlling at least one gas outlet and/or at least one gas inlet of said gas zone whereby the amount, or partial pressures, and flows of gases to and from the gas zone which makes up the pressure can be controlled.

Generally, the selected pressure depends on the plasma generation conditions of the gas and desired extent of plasma to be generated in the gas.

In a preferred embodiment, said pressure is in the range including 10 to 200 Pa, preferably 20 to 100 Pa, more preferably 30 to 80 Pa, most preferably 40 to 70 Pa, and in particular about 50 Pa whereby conditions ranging from a small extent of plasma in the gas to a full extent of

plasma through out the gas zone can be obtained, e.g. for use in electrode cleaning in presence of objects to be plasma treated using a small extent of plasma around the electrodes. Subsequently such objects can be treated with a larger extent of plasma extending to include the objects and plasma deposition by applying appropriate potential differences and/or pressures, typically lower potential differences and lower pressures.

In another preferred embodiment, said pressure is in the range including 0.1 to 50 Pa, preferably 1 to 30 Pa, more preferably 2 to 20 Pa, most preferably 5 to 10 Pa whereby conditions of a larger extent of plasma can be obtained at relatively low voltages, e.g. in applications of plasma deposition.

"Potential difference"

Generally, the potential difference can be generated by various power supply sources, e.g. a dc source, an ac source, or a pulsed electrical source. For a continuous dc or ac source, the potential difference can be defined by the root mean square voltage difference between the two electrodes. For a pulsed electrical source the potential difference can be based on the root means square potential difference during the pulse. Especially a pulsed electrical source can be a pulsed dc- or ac-electrical source, e.g. a pulsed RF-voltage with a given duty cycle.

In a preferred embodiment, said potential difference is in the range including 200 to 2000 V, preferably 400 to 1500 V, more preferably 600 to 1200 V, most preferably 600 to 1100 V, and in particular 600 to 1000 V whereby a relatively high energy plasma is obtained, e.g. for use

in applications of electrode cleaning. For relatively high pressures, conditions of a relatively small extent of plasma can be obtained.

In another preferred embodiment, said potential difference is in the range including 200 to 2000 V, preferably 200 to 1200 V, preferably 300 to 800 V, more preferably 300 to 700 V, and most preferably 300 to 600 V whereby a relatively low energy plasma extent is obtained, e.g. for use in applications of plasma deposition. For relative low pressures conditions of a larger extent of plasma can be obtained, e.g. in applications of plasma deposition.

The potential difference may be stable on same level (average level if it is a pulsed plasma) during the plasma treatment and/or optional cleaning of one or more electrodes, or it may preferably be varied to provide a desired plasma treatment and/or cleaning profile. In one embodiment the potential difference is higher in a step of plasma treating an object, that in a step of cleaning one or more electrode within the plasma reaction chamber.

The power supply for generating the potential difference between said two electrodes can be any suitable power source known in the art.

In a preferred embodiment, said potential difference is generated by power supply comprising: a direct current (DC) power supply, an alternating current (AC) power supply: at sub-radio frequencies, including main frequencies (50-60 Hz), low frequencies (LF), and audio frequencies (AF); at radio frequencies (RF), and at microwave frequencies (MW).

In a preferred embodiment the potential difference is generated by AC power with frequencies at 50-60 HZ.

More details of the power supply are disclosed together with the description of the apparatus, the description of which is incorporated in this part of the description by reference.

"Plasma power density"

Generally, the energy available in the plasma is provided by application of a given potential difference for a suitable period of time to provide the necessary power consumption of the plasma depending on the application.

In a preferred embodiment, said potential difference and said gas zone are adapted to provide a plasma power density in the range including 0.01 to 100 W/l, preferably 0.1 to 10 W/l, more preferably 0.1 to 5 W/l, most preferably 0.1 W/l to 3 W/l, and in particular about 1 W/l whereby plasma power densities suitable for various plasma treatments, e.g. etching and/or deposition in the gas zone, within the extent of plasma of a suitable volume can be obtained.

For a continuous dc or ac source, the plasma power density can be expressed as the average power consumption of the plasma divided by the volume over which the plasma exists. For a pulsed electrical source the plasma power density can be expressed as the average power consumption of the plasma during the pulse divided by the volume over which the plasma exists.

In plasma with a limited extent, the volume over which the plasma exists is difficult to measure. Further more, the inhomogeneous nature of plasma with a limited extent makes it more preferable to speak about average plasma power density. The average plasma power density is the average power consumption in the plasma divided by the maximum volume in which the plasma can exist in the used geometry.

"Electrode configuration"

Generally, the at least two electrodes are configured to provide conditions at which energy can be transferred to the gas comprising a plasma generating component.

In a preferred embodiment, the configuration of said at least two electrodes comprises at least one of: mutual distance, individual shapes, and mutual orientation whereby the distribution of generated plasma and the extent thereof can be controlled to provide a desired pattern; the primary mechanism is anticipated to be by modification of the electrical fields generated by the electrodes.

Generally, the at least two electrodes can be arranged in direct contact with the gas or not. In case they are not in contract with the gas, they induce energy in the gas, usually through a container wall.

In one embodiment, said at least two electrodes are arranged inside said gas zone, and/or outside said gas zone whereby plasma can be generated in the gas zone.

In one preferred embodiment, one two or more electrodes are arranged inside the same reactor as the plasma, and in contact with the plasma during treatment of an object, the configuration of electrodes being so that the plasma in the electrode cleaning step does not contact the object even though the object is still in the same reactor.

In a preferred embodiment, the at least two electrodes are in form of concentric electrodes, optionally one of said electrodes being in the form of a grid. In the case of concentric electrodes, plasma is generated in the volume defined by the outer electrode. When the electrodes are arranged inside the gas zone, electrode contamination can occur, requiring subsequent electrode cleaning in order not to contaminate subsequent plasma treatments.

"Additional modification of extent of plasma"

Generally, the extent of plasma can be modified by inducing electric or magnetic fields in the plasma, or by affecting the plasma by insertion of additional objects such as shields or masks.

In a preferred embodiment, the extent of plasma is modified by introducing an additional electrical field, a magnetic field, and/or a shield whereby the shape and/or the pattern of the extent of plasma can be modified.

The shielding mechanism which affects the plasma can be any suitable physical or chemical mechanism, e.g. based on absorption, reflection or deflection of the plasma.

In a preferred embodiment, said shield is selected from the group comprising absorbers, reflectors, deflectors and masks whereby various means for modifying the extent of plasma can be applied.

"Shielding material"

Generally, the material used for the shield is selected for its physical properties, including electrical and mechanical properties such as insulating ability, strength and form stability under vacuum and plasma conditions.

In a preferred embodiment, said absorbers, reflectors, deflectors or masks comprise a material selected from the group comprising metallic, preferably stainless steel; non-metallic, preferably glass; and insulating materials, preferably glass, ceramic, and a polymeric material, including rubber, and thermoplastic materials, preferably polyethylene(PE), Polypropylene(PP), polyvinylchloride(PVC), polyamide(PA), polyvinyldifluoride(PVDF), and carbon-filled polyethylene; other polymer materials, including non-thermoplastic polymers, preferably polyesters; and combinations thereof whereby the material can be chosen to be stable in the plasma at the energy and pressure applied, e.g. for low energy plasma, thermoplastic materials with relatively low glass transition temperatures can be used without being deformed.

"Objects in the plasma - also called substrates"

In a preferred embodiment, said extent of plasma is adapted so that at least one object arranged in said gas

zone is wholly or partly exposed to, or not exposed to said plasma.

In a preferred embodiment, said at least one object comprises: a substrate; a substrate holder; a sensor, preferably a deposition monitoring sensor, or a plasma intensity sensor; and a sputtering electrode whereby specific objects which may or may not affect the generated plasma can be exposed to the plasma, or not.

"Substrate position"

In a preferred embodiment, the position of said substrate, said substrate holder, and said sensor holder with respect to one of said at least two electrode is so that the normalized substrate position ϕ is in the range including 0.3 to 1, preferably including 0.5 to 1, more preferably including 0.9 to 1 whereby an optimal position of the substrate can be defined for e.g. concentric electrodes. Fore a more detailed discussion of ϕ see the description in relation with Fig. 3.

"Measurement of extent of plasma"

The extent of plasma can be measured by any suitable technique, e.g. optical or electrical.

In a preferred embodiment, said extent of plasma in said gas zone is determined by direct measurement whereby adjustment of the extent of plasma can be obtained during operation, e.g. for providing complex etching or deposition patterns.

Generally, the extent of plasma need not be determined by direct measurement.

In a preferred embodiment, said extent of plasma in said gas zone is determined by a priori calibration whereby plasma etching or plasma deposition can be performed under fixed conditions and fixed positions of electrodes and objects e.g. substrates, without requiring plasma sensing equipment present in the gas zone for measuring the extent of plasma.

More details of the measurement of extent of plasma are disclosed together with the description of the apparatus, the description of which is incorporated in this part of the description by reference.

"A plasma treatment apparatus with controlled extent of gas plasma"

In another aspect, according to the present invention, these objects are fulfilled by providing an apparatus for plasma treatment with controlled extent of gas plasma, the apparatus comprising:

(A) a gas section, said gas section comprising at least one gas inlet and at least one gas outlet adapted for providing a gas having a pressure;

(B) at least two electrodes, said at least two electrodes being configured to wholly or partly encompass said gas section;

(C) at least one power supply, said at least one power supply supplying a potential difference between at least

two of said at least two electrodes for generating a plasma in said gas section;

(D) at least one plasma measuring means for measuring the extent of the plasma in said gas section with respect to at least one of said at least two electrodes; and

(E) at least one controlling means for controlling the extent of said generated plasma; said at least one controlling means being adapted to control at least one of: said gas, said pressure, said potential difference, and said configuration of said at least two electrodes in response to a measurement of said at least one plasma measuring means;

whereby plasma treatments with controlled extent of plasma can be performed.

Preferred embodiments are defined in the dependent claims defining corresponding means to those described for the preferred actions of the method according to the invention.

"Type of gas, composition, and amounts"

In a preferred embodiment, said at least one controlling means comprises means for controlling the type of said gas, its composition, and/or the amount of its components whereby the extent of plasma can be controlled when conditions for generating a plasma change with respect to the type of gas, its composition, and amount, or partial pressures, e.g. wherein the conditions for generating a plasma in a mixture of Ar and N_2O for etching application are changed as the etching gas is exchanged with a

deposition gas comprising He and the selected monomer for plasma polymerisation deposition.

In a preferred embodiment, said gas section contains a gas component or a gas composition selected from the group comprising:

inert gasses, including noble gasses, preferably He, Ar, Ne, Xe;

oxidizing gasses, preferably O_2, NO_2, N_2O, CO_2;

halogen gasses, preferably Cl_2, F_2;

and reducing gasses, preferably H_2 and NH_3;

mixtures of said noble gasses with said halogen gasses, said oxidizing gasses, or with said reducing gasses;

a mixture of said halogen gasses with said oxidizing gasses, or with said reducing gasses; and

plasma polymerisable substances, including monomers, preferably selected from the group consisting of aliphatic hydrocarbons, including C_1–C_{16} alkanes such ethane, hexane ; C_2–C_{16} alkenes such as hexene, 1-hexene, 3-methyl-1-hexene, dienes such as 1,4-hexadiene, butadiene), 1,4-hexadiene; C_2–C_{16} alkynes including hexyne, 1-hexyne; aromatic hydrocarbons, including styrene, benzene; substituted benzenes; aromatic monomers of styrene compounds; monomers of vinyl compounds, including vinylpyrrolidone; acrylate compounds including methylacrylate, acrylonitrile, glycidylmethacrylate, methacrylacid-anhydride, and acrylic acid chloride,

and mixtures of said polymerisable substances and said inert gasses, halogen gasses, oxidizing gasses and reducing gasses;

whereby control of extent plasma in gasses for treatment in etching and cleaning with inert gases, oxidizing gasses, reducing gasses, or mixtures thereof, and in gasses for plasma polymerisation with polymerisable substances can be obtained.

In a preferred embodiment, said at least one controlling means comprises means for controlling at least one gas outlet, preferably a reduction valve controlled by a pressure controller and a pressure transducer, and/or means to control at least one gas inlet, preferably a flow controller, said means for controlling said gas outlet and said gas inlet preferably being controlled by a computer; whereby the amount and flow of gas can be controlled.

"Gas pressure and vacuum pump"

In a preferred embodiment, said pressure is in the range including 10 to 200 Pa, preferably 20 to 100 Pa, more preferably 30 to 80 Pa, most preferably 40 to 70 Pa, and in particular about 50 Pa; whereby conditions of a limited extent of plasma can be obtained, e.g. for use in applications of electrode cleaning in presence of substrates.

In a preferred embodiment, said pressure is in the range including 0.1 to 50 Pa, preferably 1 to 30 Pa, more preferably 2 to 20 Pa, most preferably 5 to 10 Pa, whereby

conditions of a larger extent of plasma can be obtained, e.g. in applications of plasma deposition.

The vacuum pump for providing a vacuum can be any suitable vacuum pump which is able to provide a vacuum of sufficient low pressure to ensure that steady homogeneous plasma can be sustained in the reaction section.

Generally, vacuum pumps comprise diffusion pumps, rotary vane vacuum pumps, rotary piston vacuum pumps, roots vacuum pumps. Cascading vacuum pumps can be applied.

On the high-pressure side, the vacuum pump is connected to a suitable exhaust gas flow system, including mechanical booster pumps, rotary pumps etc.

It is preferred that the pressure can be controlled in a control loop comprising a pressure gauge, an electronic controller device, e.g. a PID controller, and an actuator connected to said electronic controller device. Said actuator may comprise a reduction valve, e.g. a butterfly valve, inserted between the vacuum pump and the vacuum chamber, or said actuator may comprise a variable vacuum pump, e.g. a roots vacuum pump.

A high vacuum chamber volume to total feed gas flow ratio ensures that minor variations in gas flow does not affect the homogeneity of the plasma.

Vacuum pumps can be coupled to the vacuum section in any suitable manner known to a skilled person, including coupling by flexible steel pipes and rigid steel pipes.

<u>"Potential difference and power supply"</u>

The potential difference and power supply may e.g. be as disclosed above for the method of the invention.

Generally, the potential difference can be caused by various power supply sources, e.g. a dc source, an ac source, or a pulsed electrical source. For a continuous dc or ac source, the potential difference can be defined as the root mean square voltage difference between the two electrodes. For a pulsed electrical source the potential difference can be defined as the root means square potential difference during the pulse. Especially the power supply can be a pulsed dc- or ac electrical source, e.g. a pulsed RF-voltage with a given duty cycle.

In a preferred embodiment, said at least one power supply comprises: a direct current (DC) power supply, an alternating current (AC) power supply which at sub-radio frequencies includes a mains frequency (50-60 Hz) power supply, a low frequency (LF) power supply, and an audio frequency (AF) power supply; and which at higher frequencies includes a radio frequency (RF) power supply, and a microwave frequency (MW) power supply.

In a preferred embodiment, said at least one controlling means comprises means for controlling said potential difference in the range including 200 to 2000 V, preferably 400 to 1500 V, more preferably 600 to 1200 V, most preferably 600 to 1100 V, and in particular 600 to 1000 V; whereby control of a relatively high energy plasma is obtained, e.g. for use in applications of electrode cleaning. For relatively high pressures, conditions of a limited extent of plasma can be obtained.

In a preferred embodiment, said at least one controlling means comprises means for controlling said potential difference in the range including 200 to 2000 V, preferably 200 to 1200 V, preferably 300 to 800 V, more preferably 300 to 700 v, and most preferably 300 to 600 V whereby a relatively low energy plasma is obtained, e.g. for use in applications of plasma deposition. For relative low pressures conditions of a larger extent of plasma can be obtained, e.g. in applications of plasma deposition.

Generally, a skilled person can adapt the applied potential difference to obtain an extent of plasma and intensity thereof by experimentation for his particular electrode configuration. A preferred electrode configuration comprises concentric cylindrical electrodes, the inner electrode being a grid, for which the plasma is homogeneously distributed. Other electrode configurations can be calibrated against this standard configuration.

For a preferred electrode configuration, the plasma power density is 0.01 to 100 W/l, however depending on the application the plasma power density can be adapted to that desired. For example, at low plasma power density functionality of monomers can be maintained during polymerisation.

In a preferred embodiment, said potential difference and said gas section are adapted to provide a plasma power density in the range including 0.01 to 100 W/l, preferably 0.1 to 10 W/l, more preferably 0.1 to 5 W/l, most preferably 0.1 W/l to 3 W/l, and in particular about 1 W/l; whereby plasma etching or deposition can be obtained.

For a continuous dc or ac source, the plasma power density can be the average power consumption of the plasma divided by the volume over which the plasma exists. For a pulsed electrical source the plasma power density can be the average power consumption of the plasma during the pulse divided by the volume over which the plasma exists.

In a preferred embodiment, the apparatus comprises at least one power supply, said at least one power supply being adapted to provide at least one alternating voltage of at least one phase to said at least two electrodes, said at least one phase of said alternating voltage being in a number equal to or less than the number of said at least two electrodes.

Preferably, the power supply supplies a sufficient electrode voltage for the plasma to ignite. Furthermore, it allows accurate control of the electrode voltage. For AC power supplies this can be achieved by connecting the electrodes of the plasma treatment apparatus to the high voltage side of step-up transformers, connecting the low voltage side of said step-up transformers to variable transformers, said variable transformers being connected to a common AC power source, e.g. the European standardised 50 Hz, 220 V power grid or the US standardised 60 Hz, 110 V power grid. The voltage set-point is set by tuning the variable transformers.

For each said one ore more phases preferably at least one conventional lamps are connected in series with said at least one electrodes to stabilise the current, I, of each phase. At low values of I the electrical resistance, R_{el}, of a lamp is low and constant with regard to I. At intermediate and high values of I, R_{el} increases with increas-

ing I. In the case that I increases rapidly, e.g., due to the formation of an electrical arc between neighbouring electrodes R_{el} will increase and thereby decrease I. This in turn will eliminate said electrical arc. Thus the non-linear current-resistance characteristic of conventional lamps can be used to effectively stabilise the plasma density in AC and DC powered plasmas.

Alternatively, the electrodes can be supplied with a direct current (DC) potential difference, preferably a pulsating DC potential difference. A pulsating DC voltage supply is preferably obtained by applying a rectification to the output of the 50Hz AC voltage supply described above. Said rectification can be obtained with a rectifier bridge consisting of four diodes.

"Electrode configuration"

The Electrode configuration may e.g. be as disclosed above for the method of the invention.

In a preferred embodiment, said at least one controlling means comprises configuration means for controlling the configuration of said at least two electrodes, said configuration means comprising distance-adjusting means for adjusting the mutual distance, preferably a telescopic expander, and/or a displaceable electrode carrier; shaping means for shaping an electrode, preferably a remotely deformable electrode, and/or a pre-shaped electrode; and orientation means for adjusting mutual orientation, preferably a rotational electrode carrier.

In a preferred embodiment, said at least two electrodes are arranged inside said gas section, and/or outside said

gas section; whereby a plasma pattern can be generated in the gas. When the electrodes are arranged inside the gas, electrode contamination can occur.

In a preferred embodiment, said electrodes are made of an electrically conductive material which is resistant to oxide formation and sputtering, preferably stainless steel.

In a preferred embodiment, said at least two electrodes comprise a circumferential electrode, preferably at least two concentric ellipsoidal electrodes.

In a preferred embodiment, one of said circumferential electrodes comprise a grid electrode, preferably the inner electrode being a grid electrode, more preferably a grid electrode having a grid size in the range including 5 to 50 mm, preferably 5 to 20 mm, more preferably about 10 mm.

"Measuring plasma extent"

In a preferred embodiment, said at least one plasma measuring means comprises inspection means for optical inspection.

In a preferred embodiment, said optical inspection means comprises means for visual inspection, preferably said visual inspection means comprises an inspection window, and for some application a telescope can be used; whereby measurements of extent of plasma can be performed external to the gas section and plasma through e.g. an inspection window. Visual inspection includes observation by the eye, or observation by means of a camera whereby

the extent of plasma can be measured with respect to e.g. a ruler placed substantially perpendicular to the electrode being inspected.

In a preferred embodiment, said inspection means comprises a plasma sensor, or a set of plasma sensors, preferably an optical sensor; or an electrical sensor, in particular an electrical sensor comprising a voltage probe and a voltmeter.

In a preferred embodiment, said at least one controlling means comprises: electrical field-generating means for generating an additional electrical field, preferably at least two electrodes positioned internally and/or externally to said gas section; magnetic field-generating means for generating a magnetic field, preferably at least one magnet, or inductive coil, positioned internally and/or externally to said gas section; and/or shielding means for wholly or partly shielding objects not to be exposed to plasma; thereby modifying the shape and/or the pattern of said predetermined extent of plasma.

In a preferred embodiment, said shielding means is selected from the group comprising absorbers, reflectors, deflectors, and masks; whereby various means for modifying the extent of plasma can be applied.

In a preferred embodiment, said shielding means comprise a material selected from the group comprising metallic, preferably stainless steel; non-metallic, preferably glass; and insulating materials, preferably glass, ceramic, and polymeric materials, including rubber, thermoplastic material, thermosetting materials, preferably polyethylene(PE), Polypropylene(PP), polyvinylchloride

(PVC), polyamide (PA), polyvinyldifluoride (PVDF), carbon-filled polyethylene, polyesters, and combinations thereof; whereby shielding means of suitable stability, including mechanical, chemical and thermal stability, in the plasma can be obtained.

In a preferred embodiment, said at least one controlling means comprises means for arranging at least one object in said gas section so that said at least one object is exposed, or not exposed, wholly or partly to said plasma.

In a preferred embodiment, said at least one object comprises: a substrate; a substrate holder; a sensor, preferably a deposition monitoring sensor, or a plasma intensity sensor; and a sputtering electrode; whereby specific objects which may or may not affect the generated plasma can be exposed to the plasma, or not.

"Substrate and other objects"

Generally, a substrate can be subjected to the generated gas plasma in any suitable way, including manually operated manipulators and positioning means inside the reaction section.

In a preferred embodiment, however, the apparatus further comprises a substrate holder, said substrate holder being adapted to receive at least one substrates for treatment by the gas plasma, and being arranged in said reaction section with respect to the electrodes to receive a predetermined plasma pattern with respect to the electrodes whereby particular reproducible plasma treatment conditions for different substrate batches and different substrates within batches can be obtained.

In another preferred embodiment, the apparatus further comprises means for adjusting the position of said substrate holder with respect to said at least one electrode whereby a more accurate and precise positioning of the substrate and consequently a more accurate treatment conditions can be obtained. In particular, the substrates can be placed with respect to the electrodes so that electrodes can be cleaned by plasma cleaning while substrates are present in the reaction section. This allows very clean plasma deposition conditions to be obtained without having to remove substrates from the reaction section. Consequently, automation and a higher throughput can be obtained.

In a preferred embodiment, the position of said substrates with respect to one of said at least two electrodes is so that the normalized substrate position ϕ is in the range including 0.3 to 1, preferably including 0.5 to 1, in particular including 0.9 to 1; whereby for e.g. concentric electrodes, an optimal position of the substrate is defined. Fore a more detailed discussion of ϕ see the description in relation with Fig. 3.

"Sluice for introducing substrates and objects"

In a preferred embodiment, the apparatus further comprising a sluice for introducing into or for removing from the gas section at least one substrate.

In a preferred embodiment, said sluice comprises an entrance sluice section, said entrance sluice section comprising a first product valve for introducing said substrate holder and/or at least one substrates therein; and

a second product valve for introducing said substrate holder and/or at least one substrate into said reaction section; a gas outlet for evacuating said entrance sluice section; and a gas inlet.

In a preferred embodiment, said sluice comprises an exit sluice section, said exit sluice section comprising a first product valve for removing said substrate holder and/or at least one substrate from said gas section; and a second product valve for removing said substrate holder and/or at least one substrate from said exit sluice section; a gas outlet for evacuating said exit sluice section; and a gas inlet.

"Use of method and apparatus with controlled extent of gas plasma"

In still another aspect, according to the present invention, these objects are fulfilled by providing use of a method or an apparatus according to the invention comprising plasma treatments and/or plasma-assisted surface modification of electrodes and substrates, preferably including plasma cleaning, plasma etching, plasma activation, and plasma deposition of electrodes, substrates, or both.

In a preferred embodiment, plasma deposition comprises plasma polymerisation, and/or metallization.

In another preferred embodiment, plasma activation comprises radical formation, and/or oxidation, or reduction.

Further uses are defined in the claims, and illustrated in the examples.

"Continuous plasma treatment apparatus"

In a still further aspect, the present invention relates to a plasma treatment apparatus, the apparatus comprising:

(A) a gas section, said gas section comprising at least one gas inlet and at least one gas outlet for providing a gas at a given pressure;

(B) at least two electrodes, said at least two electrodes being configured to wholly or partly encompass said gas section;

(C) at least one power supply, said at least one power supply supplying a potential difference between at least two of said at least two electrodes for providing a plasma in said gas;

(D) a sluice for introducing and/or removing a least one substrate into and/or from said gas section, whereby continuous plasma treatments can be perform at a series of substrates without shutting down the plasma and thereby increasing the plasma treatment productivity.

In a preferred embodiment, said sluice comprises an entrance sluice section, said entrance sluice section comprising a first product valve for introducing said substrate holder and/or at least one substrates therein; and a second product valve for introducing said substrate holder and/or at least one substrate into said gas section; a gas outlet for evacuating said entrance sluice section; and a gas inlet.

In another preferred embodiment, said sluice comprises an exit sluice section, said exit sluice section comprising a first product valve for removing said substrate holder and/or at least one substrate from said gas section; and a second product valve for removing said substrate holder and/or at least one substrate from said exit sluice section; a gas outlet for evacuating said exit sluice section; and a gas inlet.

Further details are as described for the apparatus with controlled extent of plasma according to the invention, incorporated in this part of the description by reference.

3. BRIEF DESCRIPTION OF THE DRAWINGS

In the following, by way of examples only, the invention is further disclosed with detailed description of preferred embodiments. Reference is made to the drawings in which

Fig. 1a shows a sketch of an embodiment of a plasma treatment apparatus with controlled extent of gas plasma according to the invention;

Fig. 1b shows a sketch of an embodiment of a plasma treatment apparatus with controlled extent of gas plasma according to the invention, comprising two electrodes, one electrode constituting a wall of a gas section;

Figs. 1c, 1d, and 1e show sketches of the gas section of an embodiment illustrating increasing plasma extent;

Fig. 1f shows a sketch of the gas section of an embodiment illustrating use of shielding means in form of a mask;

Figs. 2a and 2b show a cross-sectional view and a longitudinal sectional view of a sketch of a preferred embodiment of a plasma treatment apparatus according to the invention;

Fig. 3 shows a cross-sectional view of a sketch of a preferred embodiment of a plasma treatment apparatus similar to that shown in Figs. 2a and 2b, illustrating definitions of extent of plasma within a gas section inside an inner electrode;

Fig. 4a shows a graph of ε_1, the normalized extent of the Faraday dark space (see Fig. 3) versus the potential difference (in Volts rms) between two electrodes of an exemplary embodiment of the plasma treatment apparatus described in example 1 at various pressures in the range of 0.5 and 10 Pa;

Fig. 4b shows a graph of ε_1 and ε_2 (see Fig. 3), defining the boundaries of the Faraday dark space and the passive dark space respectively versus the potential difference (in Volt rms) between two electrodes of an exemplary embodiment of the plasma treatment apparatus described in example 1 at intermediate pressures (13 and 20 Pa);

Fig. 4c shows a graph of ε_1 (see Fig. 3), defining the boundaries of the passive dark space respectively versus the potential difference (in Volt rms) between two electrodes of an exemplary embodiment of the plasma

treatment apparatus described in example 1 at high pressures (50 and 100 Pa);

Fig. 4d shows plots of the total electrical power (in Watt) consumed versus the electrode potential difference (in Volt rms) between two electrodes of an exemplary embodiment of the plasma treatment apparatus described in example 1 at various pressures;

Fig. 5a shows a bar chart of the relative peak height of selected peaks observed in infrared absorption spectra of plasma deposited coatings before (A, B) and after (A´,B´) plasma electrode cleaning carried out at 5 Pa and at distances of 10, 30 and 70 mm from the inner electrode of an exemplary embodiment of the plasma treatment apparatus described in example 1 ;

Fig. 5b shows a bar chart of the relative peak height of selected peaks observed in infrared absorption spectra of plasma deposited coatings before (A, B) and after (A´,B´) plasma electrode cleaning carried out at 50 Pa and at distances of 10, 30 and 70 mm from the inner electrode of an exemplary embodiment of the plasma treatment apparatus described in example 1;

Fig. 6 shows a digital photo of stacks of untreated glass slides (labelled "UBEHANDLET") and glass slides exposed to plasma electrode cleaning treatment at 5 and 50 Pa, labelled "5 Pa" and "50 Pa", respectively;

Fig. 7a shows a cross-sectional view along line a-a of the sketch shown in Fig. 7b of an embodiment of a plasma treatment apparatus according to the invention;

Fig. 7b shows a longitudinal sectional view along line b-b of the embodiment shown in Fig. 7a comprising an embodiment of a plasma treatment apparatus with plasma measuring means;

Fig. 8a shows a graph of the normalized plasma intensity I versus the normalized substrate position ϕ at different vacuum pressures for pressures $P \leq 30$ Pa, measured with the plasma sensor of an exemplary embodiment of a plasma treatment apparatus shown in Figs. 7a and 7b;

Fig. 8b shows a graph of the normalized plasma intensity I versus the normalized substrate position ϕ at different vacuum pressures for pressures $P > 30$ Pa, measured with the plasma sensor of an exemplary embodiment of a plasma treatment apparatus shown in Figs. 7a and 7b; and

Fig. 9 shows a graph of the normalized plasma intensity I versus the normalized substrate position ϕ at different potential differences between the electrodes, measured with the plasma sensor of an exemplary embodiment of a plasma treatment apparatus shown in Figs. 7a and 7b.

4. DETAILED DESCRIPTION

Fig. 1a shows a sketch of an embodiment of a plasma treatment apparatus with controlled extent of gas plasma according to the invention.

The plasma treatment apparatus, here shown in a cross-sectional view, comprises: a gas section 110, corresponding to the gas zone for the method of controlling the extent of gas plasma according to the invention, here said gas section being located inside a wall 115 of a

vacuum chamber extending to the interior thereof through openings 145.

The gas section comprises at least one gas outlet 120 for letting out gasses there from, said at least one vacuum outlet preferably being connected to at least one vacuum pump, here illustrated by a pressure controlled vacuum pump 121 and a pressure reduction valve 122 for controlling the outlet of an exhaust gas 123. Further more, the gas section comprises at least one gas inlet 130 for supplying at least one gas thereto, here illustrated by a flow controller FC 131 controlling a feed gas 132.

The gas section comprises at least two electrodes 150 configured to wholly or partly encompass said gas section and arranged to generate plasma therein; here three electrodes are schematically illustrated. In this embodiment, the wall 115 of the vacuum chamber is shielded from the plasma, here by a shielding means 141 comprising vacuum openings 145 to provide fluidic communication with said gas inlet and gas outlet. Further, the gas section comprises at least one detectors 160 for detecting the extent 161 of plasma with respect to the at least two electrodes 150; here detectors are illustrated by plasma sensors, e.g. electrical plasma sensors measuring charge build-up at various distances from each of the three electrodes (not shown in details). The gas section further comprises a substrate holder 170 with substrates 171 to be treated in the plasma treatment apparatus.

The apparatus comprises at least one power supply 155 adapted to provide at least one voltage difference between at least two of said at least two electrodes for generating a plasma in said gas section, here said at

least one power supply is adapted to provide at least one voltage difference of at least one phase to the at least two electrodes 150, here schematically illustrated by three electrodes being supplied by three alternating current power supplies.

Generally the number of phases of the power supply is less than or equal to the number of electrodes whereby it is ensured that for any number of electrodes at least one phase for one electrode differs from the phases of the other electrodes, i.e. there always exists a voltage difference between at least two electrodes, whereby it is obtained that the plasma is always activated or "turned on", provided that the chosen pressure and voltage amplitude allow generation of plasma.

Alternatively, or in combination with the alternating current power supply, at least one direct current power supply can be applied. If one direct current power supply is applied at least one of the at least two electrodes must be at a different voltage, e.g. grounded.

The apparatus further comprises at least one controlling means for controlling the extent of plasma, here comprising a controller C,PC,FC for controlling the at least one vacuum outlet 120, gas inlet 130 and power supplies 155 in response to a signal from the detectors 160; here a pressure transducer PT,190 measures the vacuum pressure in the gas section. A measuring signal is transferred to a pressure controller PC,191 which controls a reduction valve 122 and a vacuum pump 121, thereby allowing the pressure in the gas section to be controlled. Further, a computer C,180 receives measuring signals from the plasma sensors 160 and pressure transducer 190 and communicates

with the gas inlet, here the flow controller FC,131, power supplies 155 and pressure set pointer 192 thereby allowing control of a predetermined extent of plasma in the gas section.

Selection of the type, composition and/or amounts of components of the gas for the gas inlet, e.g. a cleaning gas or a plasma deposition gas, also allow the extent of plasma to be controlled, such selection often involving calibration of the selected parameters and the effects achieved using method known to a skilled person.

The plasma, reactants, and substrates react, typically on exposed inner and outer surfaces of objects within the gas section, e.g. the electrodes, the substrates, or both depending on the extent of plasma.

Fig. 1b shows schematically an embodiment of the apparatus in which two electrodes are used, the vacuum wall being one of the two electrodes. The apparatus comprises a gas section 110, which is located inside a wall 151 of a vacuum chamber; a power supply 155 supplies a voltage to said vacuum chamber creating a potential difference between said wall 151 and an electrode 154 in the gas section, said electrode also being connected to a power supply 155. The apparatus further comprises a gas inlet 130, a gas outlet 120, and additional equipment as described for the apparatus shown in Fig. 1a, but not shown in Fig. 1b. A shielding means 142 electrically insulates the vacuum chamber wall from its environment.

By applying a voltage difference between vacuum chamber wall and said one electrode, and adjusting pressure and said voltage, the extent of plasma 161 can be controlled.

In this way it can be chosen to expose or not expose substrates 171 present on product tray 170 to the plasma, optionally further using shielding masks to determine the exposure pattern.

Figs. 1c, 1d, and 1e show sketches of an embodiment of the gas zone 112 illustrating "average fields", sketches of increasing plasma extents 161 by varying the parameters of pressure P_1, P_2, P_3 and voltage U_1, U_2, U_3. The dashed line determines the outside boundary of the part of the gas section where plasma can diffuse freely. In a preferred embodiment this boundary comprises a shielding means, e.g. a glass cylinder or a polymer sheet. The shaded areas 161 indicate the extent of plasma with respect to the nearest electrode 150. A lower vacuum pressure P will generally, for a given voltage U, yield a higher extent of plasma. Likewise, a higher voltage U will generally, for a given pressure P, yield a higher extent of plasma. At $P_1>P_2>P_3$ for a given voltage, or equivalently at $U_1<U_2<U_3$ for a given pressure, the plasma extents over larger distances from the plasma generating electrodes 150, i.e. the extents of plasma increase. In Fig. 1c, the extent of plasma does not reach out to and therefore does not significantly affect the substrates 171 on product tray 170. In Fig. 1d, the extent of plasma reaches out to and begins affecting the substrates. In Fig. 1e, the extent of plasma fully occupies the gas section 112 and fully affects the substrates.

Fig. 1f illustrates the use of a shielding means as a mask 143 for creating a pattern on a substrate 171. The substrate 171 is placed on a product tray 170 in gas zone 112 comprising a plasma with a maximal extent 161 generated by 3 electrodes 150. The substrate 171 is partly

shielded by a mask 143. As a result, parts of the substrate are not affected by the plasma 173, while other parts are affected by the plasma 174.

Figs. 2a and 2b show a preferred embodiment of a plasma treatment apparatus according to the invention. Fig. 2a shows a cross-sectional view along line a-a, and Fig. 2b shows a longitudinal sectional view along line b-b.

The plasma apparatus comprises a vacuum chamber 215 surrounding a gas section 210. An electrical insulation 241, here exemplified by a polyester film, surrounds an outer electrode 252 and an inner electrode 253, the outer electrode and inner electrode preferably being open concentric electrodes comprising an electrically conducting material, e.g. a metal such as stainless steel, or a conductive polymer; the electrodes are connected to a power supply, here illustrated by an AC power supply creating a potential difference between both electrodes.

The inner electrode surrounds a product tray 270 with substrate holders 272 and substrates 271. The product tray is positioned in the horizontal symmetry plane of the inner electrode at a distance $R=R_0$ from the upper surface of the inner electrode.

At least one gas inlets provide supply of at least one gases to the gas section, here illustrated by a terminal end of a gas feed pipe 233 positioned close to the product tray in the reaction section, see Fig. 2b.

At least one gas outlet 220 regulates the pressure in the gas section 210, e.g. for providing a sufficiently low

pressure in the gas section for enabling generation of a plasma.

In a preferred embodiment, the plasma apparatus further comprises an entrance sluice chamber 216 surrounding an entrance sluice section 211 for receiving substrates, substrate holders, product trays, or all of these, from the exterior via an exterior sluice port 276 and delivering thereof to the gas zone 210 through an interior sluice port 277; and an exit sluice chamber 217 surrounding an exit sluice section 212 for receiving the treated substrates, substrate holders, product trays, or all of these, via an internal sluice port 278 and delivering thereof to the exterior via an external sluice port 279. Both the entrance and exit sluice chambers comprises vacuum outlets 221, 222 for evacuation of the respective entrance and exit sluice sections.

The plasma apparatus has an inspection window 262 for visually observing the extent of plasma.

<u>"Operation mode"</u>

In automatic mode operation, a preferred plasma deposition sequence comprises actions of:

1) introducing substrates into the entrance sluice section 211 and providing a vacuum pressure, typically in the range of 0.1 - 100 Pa, optionally letting out treated substrates from the exit sluice section 212;

2) introducing substrates from the entrance sluice 211 into the gas section (or gas zone) 210, optionally

letting out treated substrates from the gas section 210 to the exit sluice section 212;

3) adjusting the extent of plasma, preferably by adjusting pressure and voltage to exclude exposure to the introduced substrates;

4) plasma cleaning interior surfaces of objects, e.g. electrode surfaces by excluding exposure of the introduced substrates, e.g. by limiting the extent of plasma, and/or by use of a shielding mask;

5) increasing the extent of plasma to include the introduced substrates;

6) introducing at least one reactant gas;

7) plasma deposition treating the introduced substrates in at least one plasma reacted gas, alone, in series, or in combination thereof; and

8) introducing new substrates into the entrance sluice section 211, optionally letting out treated substrates from the exit sluice section as defined under action (1).

"Plasma intensity zones"

Fig. 3 shows a cross-sectional view of a sketch of a preferred embodiment of the plasma treatment apparatus similar to that shown in Figs. 2a and 2b, illustrating definitions of plasma intensity zones within the section defined by the inner electrode.

ϕ denotes a normalized position with respect to the electrode, in this case the position R is normalized with respect to a characteristic length R_0 of the electrode geometry. Here R_0 is defined as the shortest distance from the surface of the inner electrode to a point or set of points inside the gas section farthest away from the electrode surface. Other ways of defining R_0 can be applied depending on the actual geometry, e.g. the characteristic length R_0 is the average distance to the electrodes.

The plasma intensity inside an inner electrode is generally not spatially homogeneous. In the section defined by the inner electrode 253, two distinct levels of plasma intensity were observed visually, depending on the distance D from the inner surface of the inner electrode towards the centre. In a zone 301 adjacent to the inner electrode and extending a distance D_1 towards the centre of the gas section, a low level of plasma intensity was observed. This zone 301, the so-called "Faraday dark space", is surrounded by the "plasma" zone 302 in which a higher level of plasma intensity is observed.

It should be noted that in direct current (DC) plasma the Faraday dark space is indeed dark and appears only at the cathode. In alternating current (AC) plasma, however, each electrode alternates to function as cathode and anode, respectively. Therefore in AC plasma the Faraday dark space is characterised by a reduced light intensity rather than by complete darkness, as the wording might indicate.

It is preferred that the extent of the Faraday dark space is expressed by a dimensionless parameter ε_1

$$\varepsilon_1 = D_1/R_0, \qquad (1)$$

wherein R_0 is a characteristic length of a given geometry of an electrode and gas section. It is given by

$$R_0 = \max\{R_{min,i}\}, \text{ for } i=1,2,3,..., \qquad (2)$$

wherein $R_{min,i}$ is the shortest distance from the i'th point in space inside the gas section volume to the electrode surface.

In other words, R_0 is here defined as the shortest distance from the surface of the inner electrode to the point or set of points inside the gas section farthest away from the electrode surface. For the inner electrode and gas section geometry of the present example, R_0 is the half of the distance between the two parallel sections of the inner electrode, here specifically R_0=70 mm was applied. Other definitions of R_0 might be applicable depending on the geometry of the electrodes.

At low pressures, here a pressure $P<13$ Pa for a preferred embodiment studied in further detail, the plasma intensity distribution could be adequately quantified by the Faraday dark space expressed by the single parameter ϕ_1. In this case, a higher intensity is visually observed in the centre inside the inner electrode.

However, at higher pressures, a further zone 303 of no or very low plasma intensity is observed. This zone, the so-called "passive dark space", is located in the centre inside the inner electrode. It is surrounded by the plasma 302; see Fig. 3. The boundary of the passive dark space

runs parallel to the inner electrode at a distance D_2 from the inner surface of the inner electrode. For convenience a dimensionless parameter for D_2 is defined,

$$\varepsilon_2 = D_2/R_0 \qquad (3)$$

For pressures P in the range from about 13 Pa to about 20 Pa for the present embodiment, the plasma intensity distribution can be described by the two parameters ε_1 and ε_2. For higher pressures D_1 becomes too small to be observed by the naked eye, i.e. $D_1<1$ mm. Thus, for practical purposes at pressures $P>20$ Pa, the plasma intensity distribution can be described by the passive dark space expressed by the single parameter ε_2.

The extent of plasma, as it can be visually observed, can be described by the dimensionless parameter ε. ε can be calculated by subtracting the extent of the Faraday dark space from the extent of the passive dark space and normalising with respect to the characteristic length of the electrode geometry R_0:

$$\varepsilon = \varepsilon_2-\varepsilon_1 = (D_2-D_1)/R_0 \qquad (4)$$

Fig. 4a shows a graph of ε_1, the normalized extent of the Faraday dark space (see Fig. 3) versus the potential difference (in Volts rms) between the two electrodes of an exemplary embodiment of the apparatus described in example 1 similar to that shown in Figs. 2a and 2b at various pressures in the range of 0.5 and 10 Pa.

It can be seen that ε_1 decreases for increasing pressures. It is further observed that ε_1 decreases for increasing potential difference, whereby a constant value

is reached at higher voltages (see example 1 for more details).

Fig. 4b shows a graph of ε_1 and ε_2 (see Fig. 3), defining the boundaries of the Faraday dark space and the passive dark space respectively versus the potential difference (in Volt rms) between the two electrodes of the exemplary embodiment mentioned for Fig. 4a at intermediate pressures (13 and 20 Pa).

It is observed that ε_1 decreases for increasing pressures and increasing potential differences. It can be seen that ε_2 is fairly constant at lower or higher potential differences, but a sudden transition is observed at intermediate potential differences, dependent on the pressure. At potential differences higher than this transition point, the plasma extents over the whole space defined by the electrodes, resulting in $\varepsilon_2=1$ (see example 1 for more details).

Fig. 4c shows a graph of ε_1 (see Fig. 3), defining the boundaries of the passive dark space respectively versus the potential difference (in Volt rms) between the two electrodes of the exemplary embodiment mentioned for Fig. 4a at high pressures (50 and 100 Pa);

It is seen that $\varepsilon_1<0,1$ at these pressures. This means that the optical intensity in the plasma can only be observed in a small volume close to the inner electrode. In terms of fig 4b, this means that at these pressures the transition point lies outside the voltage range used (see example 1 for more details).

The boundary of areas with different intensity is a gradual one. The figures shown are therefore solely meant to indicate that the spatial distribution of the optical intensity of plasma on voltage and pressure.

Fig. 4d shows plots of the total electrical power (in Watt) consumed versus the electrode potential difference (in Volt rms) between two electrodes of the exemplary embodiment mentioned for Fig. 4a at various pressures;

It can be seen that the power increases with increasing pressure and with increasing voltage in the full range of pressures and voltages applied, indicating a increase in power consumption and thus electrical resistance in the plasma (see example 1 for more details).

Fig. 5b shows a bar chart of the relative peak height of selected peaks observed in infrared absorption spectra of plasma deposited coatings before (A, B) and after (A´,B´) plasma electrode cleaning carried out at 5 Pa and at distances of 10, 30 and 70 mm from the inner electrode of an exemplary embodiment of example 1.

For the upper plate (10 mm) all peaks in the difference spectrum had disappeared (no absorption for the peaks A′ and B′ at 10 mm in Fig. 5a indicating that the organic thin film had been completely removed from the surface of this plate during the plasma cleaning. For the middle plate (30 mm) and lower plate (70 mm), the removal of organic film was less complete at both peaks. The absorption peaks in the difference spectra of these two plates had been reduced in height but not completely eliminated.

Fig. 5b shows a bar chart of the relative peak height of selected peaks observed in infrared absorption spectra of plasma deposited coatings before (A, B) and after (A´,B´) plasma electrode cleaning carried out at 50 Pa and at distances of 10, 30 and 70 mm from the inner electrode of an exemplary embodiment of example 1.

The same general trends that were observed in figure 5a can be observed in fig. 5b, i.e. the effectiveness of the plasma cleaning decreases at increasing distance from the inner electrode. The main difference is the overall effectiveness of the cleaning plasma, which is considerably lower at 50 Pa. In fact the thickness of the organic thin film on the lower plate appears to have been decreased only very little during the high-pressure plasma cleaning, if at all.

Fig. 6 shows a digital photo of stacks of untreated glass slides (labelled "UBEHANDLET") and glass slides exposed to plasma electrode cleaning treatment at 5 and 50 Pa, labelled "5 Pa" and "50 Pa", respectively;

The glass slides present in the high pressure electrode cleaning were not discoloured compared to the untreated ones, while the slides subjected to a low pressure electrode cleaning process show a discolouration.

Fig. 7a shows a cross-sectional view along line a-a of the sketch shown in Fig. 7b of an embodiment of a plasma treatment apparatus according to the invention.

Fig. 7b shows a longitudinal sectional view along line b-b of the embodiment shown in Fig. 7a comprising plasma measuring means.

The plasma treatment apparatus comprises a vacuum chamber wall 215 surrounding a gas section 710. The plasma apparatus comprises an outer electrode 752 and an inner electrode 753, the outer electrode and inner electrode preferably being open concentric electrodes, comprising a suitably mechanically stable electrical conductor e.g. of stainless steel; the electrodes are connected to a power supply, here illustrated as an AC power supply creating a potential difference between both electrodes.

The vacuum chamber wall is shielded from the plasma phase by a shielding means, here a polyester film (0.125 mm, Linatex) surrounding the outer electrode 152 and covering the top and bottom of the plasma chamber 715.

A gas inlet 730 and gas feed tube 733 provide supply of the feed gases to the gas section.

The gas outlet 720 is connected to a vacuum pump to provide vacuum in the vacuum chamber.

The plasma apparatus has an inspection window 762 for visually observing the extent of plasma.

The plasma apparatus comprises a six-channel plasma sensor, mounted on the substrate holder 763 inside the inner electrode 753. The construction of this sensor is described in example 5 below.

Fig. 8a shows a graph of the normalized plasma intensity I versus the normalized substrate position ϕ at different vacuum pressures for pressures $P \leq 30$ Pa, as measured with

the plasma sensor of an exemplary embodiment of a plasma treatment apparatus shown in Figs. 7a and 7b.

It can be observed, that the measured plasma intensity, normalised to its maximum value (as shown in Fig. 9), is lower in the Faraday dark space, but only becomes negative for the lowest pressure value. At these pressures, the plasma intensity is relatively homogeneous in the centre of the concentric electrodes. The point at ϕ=0.81 is the signal of the reference probe, shielded from the plasma by ceramic shielding means 744.

Fig. 8b shows a graph of the normalized plasma intensity I versus the normalized substrate position ϕ at different vacuum pressures for pressures P>30 Pa of an exemplary embodiment of a plasma treatment apparatus shown in Figs. 7a and 7b.

It can be seen that at higher the plasma intensity falls at longer distances from the inner electrode. This shows visually as a passive dark space. At pressures P>200 Pa, a plasma could not be generated under the current conditions.

Fig. 9 shows a graph of the normalized plasma intensity I versus the normalized substrate position ϕ at different potential differences at the electrodes and a pressure of 40 Pa of an exemplary embodiment of a plasma treatment apparatus shown in Figs. 7a and 7b.

The plasma intensity at this pressure is shown to increase with higher potential difference between the electrodes.

5. EXAMPLES

Preferred embodiments of the invention are illustrated by the following examples.

EXAMPLE 1 "Control of extent of plasma"

In this example, the extent of plasma as a function of pressure and voltage is measured by visual observations. An apparatus as outlined above and shown in Figs. 2a and 2b, but without sluices, was used. The apparatus consisted of a gas section constituted by a 300 L cylindrical vacuum chamber with a diameter of 60 cm, with a stainless steel wall, and provided with a substrate feed port at one end and a gas outlet at the other end.

The port was a stainless steel circular door comprising a vacuum flange with a diameter of 60 cm. The port had a glass inspection window with a diameter of 10 cm, giving the possibility of optical inspection.

The gas outlet was connected to a vacuum pump and pressure regulation system, as illustrated in fig. 1a.

The gas section was equipped with an electrode system similar to that illustrated in Figs. 2a and 2b, showing a front cross-sectional view and a side longitudinal view, respectively. The electrode geometry comprises two electrodes: an outer electrode and an inner electrode surrounded by the outer electrode, said electrodes being substantially concentric.

In this embodiment, the outer electrode consists of a stainless steel plate of thickness 0.5 mm formed as an

ellipsoidal tube with an approximately elliptical cross section having a width of 540 mm, a height of 240 mm, and length of 1000 mm. The outer electrode constitutes a volume of approximately 135 litres.

The outer electrode is tightly wrapped in a clear polyester film (0.125 mm, Linatex), functioning as a shield to limit the extent of plasma at the outside of the outer electrode 152. It is preferred that this polyester film extends over the full length of the cylindrical chamber for shielding of the inside of the chamber walls from the plasma thereby reducing contamination and risk of spark generation.

The inner electrode consists of a stainless steel grid of thickness 1 mm and grid size 1 cm, formed as an ellipsoidal tube with an approximately elliptical cross section, width of 360 mm, height of 140 mm, and length of 1000 mm.

The potential difference between the electrodes was supplied by a 50 Hz AC power supply comprising a step-up transformer, a variable transformer, and a current stabilizer. The electrodes were connected to the high voltage side of step-up transformers, here Nordelettronica (230V rms/50Hz to 700V rms). The low voltage side of said step-up transformers was connected to variable transformers, said variable transformers, here Lübcke (220V rms to 0-220V rms), each being connected to one of the phases of a common AC power source, here mains of the European standardised 50 Hz, 220 V power grid. The voltage set-point is set by tuning the variable transformers.

To each electrode, a current stabilizer is connected, here a set of lamps connected in series to stabilise the electrical current of each phase. Said set of lamps comprising two conventional lamps (each 230V/150 W, Osram), connected in parallel, i.e. 300 W per electrode.

Similar power supplies were disclosed in International Application No. WO 02/95895 (PCT/DK01/00714) the content of which is incorporated herein by reference.

A ruler of length 70 mm and width 10 mm was cut from a sheet of cardboard and placed vertically on a substrate holder, here positioned on a product tray, comprising a stainless steel grid electrically insulated from the electrodes, and placed at the horizontal symmetry-plane of the inner electrode. The ruler extended the distance from the substrate tray to 1 mm below the upper part of the inner electrode.

The feed gas, here argon (see further below), was fed through a feed gas pipe 273 terminating at a distance of 400 mm from the product tray.

The flow values were set-point values in "standard cubic centimetres per minute" (sccm) for the mass flow controllers used, here Smart Mass Flow 5850S (Brooks Instruments). The flow controllers were calibrated against argon flow standards in the range 0-500 sccm.

Argon was fed to the gas section at a flow rate of 10 sccm and a potential difference was supplied to the electrodes, using various voltage set-point values at the variable transformers. The resulting potential difference between the two electrodes comprised a 50 Hz AC potential

difference with root mean square values in the range 280 V to 1120 V.

For this electrode geometry and power supply average plasma power density values in the range of 0.01 W/l to 7.5 W/l were obtained.

During the experiments, the pressure was regulated by controlling the gas outlet using a butterfly valve. The vacuum pumps used were a roots blower and a rotary vane pump (Edwards, EH500 and E2M80, respectively).

At various potential differences and pressures, the extent of plasma was monitored. This was done by visual observing the spatial distribution of the optical intensity in the plasma with respect to the cardboard ruler through the inspection window. Only the plasma distribution in the gas section inside the inner electrode is considered in this example.

The observations were normalized and expressed as ε_1 or ε_2, according to the illustration in Fig. 3 and the description above.

At all used parameters, the potential difference between the electrodes and the total average electrical power consumption were measured directly over the electrodes.

Figs. 4a, 4b, and 4c show the experimentally observed dependencies of ε_1 and ε_2 with respect to the pressure and potential difference.

Fig. 4a shows ε_1, the normalized extent of the Faraday dark space (see Fig. 3) versus the potential difference

(in volt rms) between the two electrodes at various pressures in the range of 0.5 and 10 Pa.

It can be seen that ε_1 decreases for increasing pressures. It is further observed that ε_1 decreases for increasing potential differences, whereby a constant value is reached at higher voltages.

Fig. 4b shows ε_1 and ε_2, defining the boundaries of the extent of the Faraday dark space and the extent of the passive dark space, respectively versus the potential difference (in Volts rms) between the two electrodes at intermediate pressures (13 and 20 Pa).

It is observed that ε_1 decreases for increasing pressures and increasing potential differences. It can be seen that ε_2 is fairly constant at lower or higher potential differences, but a sudden transition is observed at intermediate potential differences, dependent on the pressure. At potential differences higher than this transition point, the plasma extents over the whole space defined by the electrodes, resulting in $\varepsilon_2=1$.

Fig. 4c shows a graph of ε_1 (see Fig. 3), defining the boundaries of the extent of passive dark space versus the potential difference (in volt rms) between the two electrodes at high pressures (50 and 100 Pa). At these high pressures, it is seen that $\varepsilon_1<0.1$. This means that the optical intensity in the plasma can only be observed in a small volume close to the inner electrode. In terms of Fig 4b, this means that at these pressures the transition point lies outside the voltage range used.

It is generally observed that the visible extent of plasma ε increases with increasing potential difference and/or decreasing pressure. At high pressures and limited extent of plasma (Fig. 4c), the same dependence of the extent of plasma on potential difference can not clearly be shown using visual observation.

Fig. 4d shows plots of the total electrical power (in Watt) consumed versus the electrode potential difference (in volt rms) at various pressures.

It can be seen that the power increases with increasing pressure and with increasing voltage in the full range of pressures and voltages applied, indicating a increase in power consumption and thus electrical resistance in the plasma.

From this example it can be concluded that the extent of plasma can be controlled by varying pressure and electrode voltage.

EXAMPLE 2 "Plasma treatments with various extents of plasma"

This example illustrates generation of plasma deposits on electrodes and samples and removal of these deposits in subsequent plasma cleaning treatment with various extents of plasma.

For a more quantitative analysis of the extent of plasma, transmission Fourier-transform infrared (FT-IR) analysis is used on plasma treated NaCl plates. The extent of plasma is estimated by placing the plates at different

distances from the electrodes during the plasma cleaning treatment.

Example 2a. "Plasma deposition on substrates and electrodes"

Substrates, here six rectangular NaCl plates of length 41 mm, width 23 mm, and thickness 4 mm, supplied by PerkinElmer were cleaned before use.

The cleaning procedure comprised using two paper towels (E-TORK paper, SCA hygiene products), immobilized on two glass plates (instrument supplied by Connecticut Instrument Corporation, Wilton, USA). One of the paper towels was wetted with a solution of 75% ethanol and 25% demineralised water. The faces of the NaCl plates were rubbed three times in a figure "8" pattern over the wet paper and subsequently this was repeated on the dry paper. This was repeated three times after which the clarity of the NaCl plates was checked. The clean and transparent NaCl plates were stored at 60 °C for drying.

The newly cleaned and dried substrates were individually analysed by transmission infrared (IR) spectroscopy in the wave number range 750 cm^{-1} to 4000 cm^{-1} using a "Spectrum 2000" Fourier-transform infrared (FT-IR) spectrophotometer, supplied by PerkinElmer.

The six substrates were placed in substrate holders on the product tray of the plasma apparatus described in example 1.

The substrates were then subjected to argon/hexene plasma deposition treatment comprising: exposure to an argon/-

hexene-plasma at a pressure of 2 Pa provided by an argon flow of 25 sccm and a hexene flow of 100 sccm; and application of an RMS voltage of 800 V at 50 Hz at an electrical power of 340 W, corresponding to an average plasma power density of 2.5 W/l, and a duration time of 480 seconds.

After the plasma deposition treatment of the substrates, both electrodes appeared yellow and less shiny than before the deposition treatment, indicating presence of a plasma-deposited layer on the electrodes.

After plasma deposition the substrates were again individually analysed by transmission FT-IR spectroscopy. Difference transmission absorption spectra of plasma deposited organic thin films were obtained by subtracting spectra of the clean NaCl-plates from the respective spectra of the coated NaCl-plates.

The chemical structure of the thin films was deduced from the difference spectra which all featured significant peaks at the following wave numbers (given in cm^{-1}): 1375, 1441, 1458, 2872, and 2932 indicating presence of methyl ($-CH_3$) and methylene ($-CH_2-$); 1625 and 1656 indicating presence of unsaturated hydrocarbon (C=C); 1705 probably indicating presence of carbonyl (C=O), and a broad peak at 3400 indicating presence of hydroxyl (-OH). In short, according to the IR spectra, the resulting thin film comprises a partially unsaturated hydrocarbon with a moderate content of oxygen. The presence of oxygen in the thin films is assumed to be caused by residual moisture (H_2O) present in the vacuum chamber at the onset of the plasma deposition.

The dominating absorption peaks by far were the ones at wave numbers 2932 and 1656. Hence only these two absorption peaks are considered in the following.

These two absorption peaks were comparable in size in the IR spectra of all six substrates, indicating a maximum extent of plasma and a homogeneous distribution of plasma at the position of the product tray, i.e. in the horizontal symmetry-plane of the ellipsoidal inner electrode.

Example 2b. "Plasma cleaning at low pressure, low power"

Three of the coated NaCl-plates were placed in individual substrate holders at different heights inside the plasma apparatus described in example 1. The upper surfaces of the plates were placed at respective distances of 10 mm (upper plate), 30 mm (middle plate), and 70 mm (lower plate) from the inner surface of the upper horizontal part of the inner electrode 153 (see Fig. 2b only showing the lowest substrate).

The three coated NaCl plates were then subjected to a low-pressure plasma cleaning treatment comprising: exposure to an argon/N_2O plasma at a pressure of 5 Pa provided by an argon flow of 30 sccm and a N_2O flow of 30 sccm; and application of an RMS voltage of 720 V at 50 Hz and an electrical power of 400 W, corresponding to an average plasma power density of 3 W/l, and a duration time of 25 minutes.

After the low-pressure plasma cleaning treatment, the electrodes appeared shiny and colourless as before the deposition treatment. This indicates that the electrodes were cleaned in the plasma cleaning process.

After the low-pressure plasma cleaning treatment, the substrates were individually analysed by transmission FT-IR spectroscopy and compared with those before the plasma cleaning. The peak heights were normalized so that the absorption peak height at wave number 2932 equals 1 for the difference spectra of the deposited thin film before cleaning.

Fig. 5a shows the relative IR absorption for the peaks 2932 cm^{-1} (A before cleaning and A′ after cleaning) and 1656 cm^{-1} (B before cleaning and B′ after cleaning) for the plates placed at distances of 10 mm, 30 mm, and 70 mm from the surface of the inner electrode.

For the upper plate (10 mm) all peaks in the difference spectrum had disappeared (no absorption for the peaks A′ and B′ at 10 mm in Fig. 5a) indicating that the organic thin film had been completely removed from the surface of this plate during the plasma cleaning. For the middle plate (30 mm) and lower plate (70 mm), the removal of organic film was less complete at both peaks. The absorption peaks in the difference spectra of these two plates had been reduced in height but not completely eliminated.

It appears from Fig. 5a that the thin film has completely disappeared at 10 mm distance from the inner electrode, at 30 mm distance the peak (A) at 2932 has almost disappeared (A′) and the peak (B) at 1656 has been moderately reduced (B′). In fact the peak (B′) at 1656 is now larger than the peak (A′) at 2932. As mentioned above the peak at 2932 stems from aliphatic structures whereas the peak at 1656 can be ascribed to unsaturated structures.

In conclusion, most of the thin organic film has been removed from the middle plate during the plasma cleaning, whereas the remainder of the organic thin film has become considerably less saturated than the original deposition thin film after plasma cleaning. The same trends are observed for the lower plate; except that both peaks A and B have become less reduced than those for the middle plate for this lower plate.

These results indicate that the extent of plasma comprises the whole inner electrode volume at the parameters used. It can be seen, however that the efficiency of plasma cleaning reduces at increasing distance from the surface of the inner electrode, showing that the plasma does not have a homogeneous intensity through out the whole volume.

Example 2c. "Plasma cleaning at high pressure, low power"

The Ar/hexene plasma deposition treatment, described in example 2a above, was repeated without substrates in the chamber. Again, this deposition process resulted in yellow and less shiny electrodes.

The three remaining coated NaCl-plates were placed in individual substrate holders at different heights as described in example 2b. The three coated plates were then subjected to a high-pressure plasma cleaning treatment comprising: exposure to an argon/N_2O plasma at a pressure of 50 Pa provided by an argon flow of 30 sccm and a N_2O flow of 30 sccm; and application of an RMS voltage of 480 V at 50 Hz and an electrical power of 340 W, corresponding to an average plasma power density of 2.5 W/l, and a duration time of 25 minutes.

After the high-pressure, low-power plasma cleaning treatment, the electrodes appeared shiny and colourless as before the deposition step. This indicates that the electrodes were in fact cleaned in the high-pressure, low-power plasma cleaning process.

After this second plasma cleaning treatment, the IR difference spectra were obtained as described above. The spectra had changed only marginally, demonstrating that plasma cleaning of the electrodes can be carried out at high pressure with minimal damage to possible substrates outside the extent of plasma, in this case in the passive dark space.

These results surprisingly show that using a higher pressure and an equal power, the extent of plasma can be adjusted to comprise a range of less than 10 mm around the electrodes. This can be used for effectively plasma cleaning the electrodes, while the samples, present at a position between 10 and 70 mm from the inner electrode are not or only marginally affected by the plasma.

In example 2d, the influence of power on the extent of plasma at high pressure is explored.

Example 2d. "Plasma cleaning at high pressure, high power"

In order to further investigate the effect of varying the electrical power on substrates inside the passive dark space the Ar/N_2O plasma cleaning treatment described above was repeated at high pressure and higher electrical power, the higher electrical power resulting from raising

the pressure while maintaining the electrode voltage setting (refer to fig. 4d).

The remaining three plasma coated NaCl-plates, not affected by the plasma treatment of example 4c, were placed in individual substrate holders at different heights as described in example 2b.

The three coated plates were then subjected to a high-pressure plasma cleaning treatment comprising: exposure to an argon/N_2O plasma at a pressure of 50 Pa provided by an argon flow of 30 sccm and a N_2O flow of 30 sccm; and application of an AC voltage of 720 V (rms) at 50 Hz and an electrical power of 700 W, corresponding to an average plasma power density of 5.2 W/l, and a duration time of 25 minutes.

After this plasma cleaning the IR difference spectra were obtained as described above and the result is presented in Fig. 5b.

The same general trends observed in Fig. 5a can be observed in Fig. 5b, i.e. the effectiveness of the plasma cleaning decreases at increasing distance from the inner electrode and there is a shift in chemical structure towards less saturation.

The main difference between the results obtained at 50 Pa compared to that obtained at 5 Pa regards the overall effectiveness of the cleaning plasma towards the substrates which is considerably lower at the higher pressure. In fact the thickness of the organic thin film on the lower plate appears to have been decreased only very little during the high-pressure plasma cleaning, if at all.

"Conclusions and discussion of examples 2a-2d"

The combined results of example 2c and 2d, shows that at relatively high pressures, the extent of plasma increases with increasing power or voltage, i.e. at a higher power, an the plasma is more effective over a larger spatial range.

The combined results of example 2a-2d illustrate that the extent of plasma can be controlled by varying the pressure and voltage. It is also shown how this can be used for cleaning the electrodes, while substrates are present in the plasma apparatus. This application is further explored in example 3 below.

EXAMPLE 3 "Glass slides in plasma electrode cleaning process"

Substrates, here 7 microscope glass slides, "G300" supplied by ProSciTech, of length 76 mm (3 inch), width 25 mm (1 inch), and thickness 1 mm were evenly distributed on the substrate tray of the plasma apparatus described in example 1 above whereby the full surface of said substrates was exposed to the environment inside the plasma apparatus.

The glass slides were subjected to relatively low-pressure plasma, with a gas composition typically used for cleaning of the plasma generating electrodes (see also example 2b above).

The glass slides were subjected to a low-pressure Ar/N_2O plasma electrode cleaning treatment comprising: exposure

to an Ar/N_2O-plasma at pressure 5 Pa, said plasma being provided by an argon flow of 30 sccm an N_2O flow of 30 sccm, an AC voltage difference of 720 V (rms) at 50 Hz, an electrical power of 400 W, corresponding to an average plasma power density of 3 W/l, and a duration of 600 seconds.

The glass slides were removed from the plasma apparatus and stacked. It was observed that the slides had achieved a faint yellow colour during the plasma cleaning. In the following this stack is referred to as "the low-pressure plasma treated slides".

The experiment was repeated with 7 fresh slides but this time at higher pressure.

The glass slides were subjected to a high-pressure Ar/N_2O plasma electrode cleaning treatment comprising: exposure to an Ar/N_2O-plasma at pressure 50 Pa, said plasma being provided by an argon flow of 30 sccm an N_2O flow of 30 sccm, an AC voltage difference of 500 V (rms) at 50 Hz, an electrical power of 400 W, corresponding to an average plasma power density of 3 W/l, and a duration time of 600 seconds.

The glass slides were removed from the plasma apparatus and stacked. No discoloration of these slides was observed. In the following this stack is referred to as "the high-pressure plasma treated slides".

Also 7 fresh slides were taken from the pack and stacked. In the following this stack is referred to as "not plasma treated slides".

The three stacks were placed next to each other on a squared piece of paper and illuminated by a fluorescent tube "PL-S 11W/827" supplied by Philips and photographed with a "CD Mavica, MVC-CD300" digital camera supplied by Sony. The resulting digital colour photo was loaded into a personal computer (PC) and the colours were balanced with the use of a computer program, "Microsoft Photo editor" supplied by Microsoft, whereby the image was made to accurately reproduce the real set-up. The tuned image was then converted to a black and white image which is shown in Fig. 6, from which it is recognised that the low-pressure plasma treated slides shown in Fig. 6(c) marked "5 Pa" are indeed darker than the high-pressure plasma treated slides shown in Fig. 6(b) marked "50 Pa". No difference in colour is observed between the high-pressure plasma treated slides and the not plasma treated slides shown in Fig. 6(a) marked "ubehandlet". This result shows that the extent of plasma can be controlled to comprise the area around the electrodes only, making it possible to carry out electrode plasma cleaning with little or no damage to possible substrates placed at a given distance from the electrodes.

This result can be used for integrating electrode cleaning and plasma deposition treatment into a single automated batch process, reducing production time as further described in example 4 below, or used in a sequence of automated batch processes.

Example 4 "DNA-slide production with integrated electrode cleaning"

International Application No. 02/053299 (PCT/DK01/00870) the content of which is incorporated herein by reference,

discloses a method for preparation of a substrate for immobilising chemical compounds and the substrate and the use thereof.

Examples 1a, 4 and 10 of said document describe plasma polymerisation of styrene as a hydrocarbon base coating and subsequently plasma polymerisation of acrylic acid chloride as a top coating.

The resulting plasma deposited organic thin film has a functionality that can be used to bind amino compounds, such as organic amino compounds, especially biological amino compounds, e.g. amino functionalised oligo-DNA, proteins, and cells.

Said functionality was measured using amine-labelled oli-go-nucleotides (oligo DNA) and their hybridisation coun-terparts, as described in example 10 of WO 02/053299.

To obtain reproducible plasma conditions, the plasma electrodes had to be plasma cleaned in a separate batch before the deposition batch. This plasma cleaning was generally performed without the presence of substrates, using low pressure and low power, such as the parameters described in example 2b and 3 in the current application.

The current example describes a similar process, whereby a hydrocarbon base coat and an acrylic acid chloride top coat are deposited. These plasma depositions are carried out in a single batch together with an electrode cleaning plasma, performed before the deposition.

"Pre-cleaning of substrates"

The substrates are microscope glass slides that were preferably pre-cleaned according to the following procedure: A rinsing solution is prepared by dissolving 50g of NaOH in 3.2 litres of de-mineralised water. The slides were washed in the solution at 70 °C for 7 minutes. The slides were then washed six times with 3.2 litres of de-mineralised water and dried at 60 °C.

"Plasma treatments"

42 pre-cleaned glass slides are then placed in a plasma treatment apparatus as described in example 1.

In this embodiment, substrates are treated on one side only by covering the other side with a cover substrate, here a microscope glass slides similar to the deposition substrate. 42 pairs of supports and substrates were evenly distributed on a product tray, comprising a stainless steel grid electrically insulated from the electrodes, and placed at the horizontal symmetry-plane of the inner electrode.

The electrodes and the substrates are subjected to five consecutive gas treatments successively providing a clean set of electrodes, a pre-treated substrate surface, a base coating on the pre-treated surface, and a top coating on the base coating, respectively:

1) N_2O/Ar-plasma cleaning treatment of electrodes: exposure to an N_2O/Ar-plasma at pressure 50 Pa, said plasma being provided by an argon flow of 30 sccm, a N_2O flow of 30 sccm, an AC potential difference between

the electrodes of 500 V (rms) at 50 Hz, an electrical power of 400 W, corresponding to an average plasma power density of 3 W/l, and a duration time of 600 s (As described in example 2, the plasma has a limited extent at these parameters. It is concentrated around the electrodes and does not come into contact with the substrates. The extent of plasma is increased for the subsequent plasma treatments by reducing the pressure.);

2) Ar-plasma pre-treatment of substrate: exposure to an Ar-plasma at pressure 1.3 Pa, said plasma being provided by an argon flow of 25 sccm, an AC potential difference between the electrodes of 1000 V (rms) at 50 Hz, an electrical power of 500 W, corresponding to an average plasma power density of 3.7 W/l, and a duration time of 60 s;

3) Ar/H_2-plasma pre-treatment of substrate: exposure to an Ar-plasma at pressure 0.013 mbar, said plasma being provided by an argon flow of 17 sccm, H_2-flow of 7 sccm, an AC potential difference between the electrodes of 1000 V (rms) at 50 Hz, an electrical power of 530 W, corresponding to an average plasma power density of 3.9 W/l, and a duration time of 60 s;

4) hydrocarbon base coating of substrates: exposure to an hexene/Ar-plasma at a pressure of 0.013 mbar, said base coating plasma being provided by an argon flow of 25 sccm, and an AC potential difference between the electrodes of 800 V (rms)at 50 Hz, an electrical power of 300 W, corresponding to an average plasma power density of 2.2 W/l, and a duration time of 15 s, and

5) poly(acrylic acid chloride) top coating of substrates: exposure to an acrylic acid chloride/Ar-plasma at a pressure 0.025 mbar, said top-coating plasma being provided by an argon flow of 25 sccm, an acrylic acid chloride flow of 200 sccm, an AC potential difference between the electrodes of 500 V (rms) of 50 cycles per second, an electrical power of 40 W, corresponding to an average plasma power density of 0.3 W/l, and a duration time of 30 s.

The treated glass slides were removed from the plasma apparatus and a new set of pre-cleaned glass slides were placed in the chamber and subjected to the five consecutive gas treatments given above.

The coated glass slides were visually inspected and no discoloration was seen. This corresponds to the results of example 3.

Slides comprising substrate materials such as silicon; polymers, such as polypropylene, polystyrene, cycloolefin-copolymers; or metals, such as stainless steel, platinum provided similar results.

"Functionality test of coatings"

The functionality of the coating was tested according to the procedure, described in example 10 of WO 02/053299 (PCT/DK01/00870) the content of which is incorporated herein by reference, yielding a similar result.

This shows that the presence of substrates to be coated in the gas section during an initial electrode plasma

treatment cleaning with a gas plasma of a limited extent does not negatively influence the performance of the subsequently applied coating. Consequently, the productivity of a plasma treatment comprising plasma cleaning and subsequent plasma deposition can be increased.

Further, a separate plasma cleaning treatment of the electrodes in a separate batch without the presence of substrates can be avoided.

<u>Example 5 "Plasma sensor using electrical charge build-up"</u>

In example 1, visual observation of extent of plasma was used to describe dependence on pressure and potential difference. In example 2, the extent of plasma was estimated on basis of FT-IR analysis on samples at various distances from the electrode.

In the present example, an alternative measure of the plasma intensity is used, namely the electrical charge build-up of objects exposed to the plasma.

In this example an embodiment of the plasma treatment apparatus according to the invention was used. The apparatus, schematically shown in Fig. 7a and 7b, comprised a gas section 710, consisting of a 30 L cylindrical vacuum chamber with a stainless steel wall 715. The chamber was equipped with a two-phase electrode system comprising two concentric electrodes: an outer cylindrical stainless steel plate electrode 752 of height 30 cm and diameter 30 cm, and an inner circular stainless steel grid electrode 753 of height 30 cm and diameter 25 cm, each electrode being connected one the two phases of an alternating cur-

rent power supply 755 operating at 50 Hz, said two phases being phase shifted 120 degrees. The power supply was comparable to the power supply described in example 1 and in EP 0 714 404, WO 00/44 207 and WO 02/35 895. The vacuum chamber wall 715 was shielded from the plasma phase by clear polyester film 741 (0.125 mm, Linatex).

The vacuum was supplied by a rotary vane vacuum pump supplied by Alcatel connected to the vacuum chamber at the vacuum outlet 720. The feed gas, here argon was supplied through a feed gas inlet 730 and gas inlet tube 733, feeding the gas into the section inside the electrodes. The vacuum chamber was electrically grounded.

A six-channel plasma sensor was made by fixing six electrically insulated flexible tinned copper wires 766 of length 30 cm and with a circular cross-section of area 0.22 mm^2, between two plane ceramic plates 763, held together with grips. From each end of the wires, 3 mm of the insulation was removed. One end of each wire was protruding from the slit between the ceramic plates at 20 mm intervals and connected to a rectangular plate of tinned copper of length 8 mm, width 6 mm, and thickness 0.25 mm, here referred to as "probes" 765. Each probe was oriented with its longest sides parallel to the slit. The probes were separated from the ceramic plates at a distance of 5 mm by spacers 764 comprising plastic (e.g. PVC, PE) cylinders of outer diameter 3 mm. The other end of each wire was connected to the low-pressure side of a vacuum proof six-pin electrical feed-through 767. On the high-pressure side of said feed-through each pin was connected to a plug by a wire 768. The probe holder 763 was supported by a substrate holder 772.

The plasma sensor was arranged inside the inner electrode 753 with the row of probes of the sensor aligned in the radial direction of the inner electrode and all probes axially positioned in the middle of the inner electrode. The outermost and the innermost probes of the sensor were positioned 3 mm and 83 mm respectively from the inner surface of the inner electrode, the remaining four probes being equally spaced of about 20 mm between the inner and the outer probe. A ceramic cylinder 744 of length 4 cm and inner diameter 8 mm was placed around the innermost probe in order to electrically shield it from the surrounding plasma. Here, the shielded probe is referred to as the "reference probe".

Plasma was sustained at the following conditions: Ar-flow 2 sccm, pressure 7.5 Pa, electrode voltage 600 V (rms), and total electrical power consumption of 63 Watt. Because of the electrical charge build-up in the plasma, a DC voltage difference, V_{probe}, between each probe and the ground was created. V_{probe} was measured for each probe, one by one with a DM-6012 digital multimeter supplied by Lutron, schematically drawn in Fig. 7b as an ideal voltmeter 781, with a unknown resistance 782 in parallel.

This experiment was repeated at various pressures, P, in the range 5 - 200 Pa. The plasma was observed through an inspection window 762 at the top of the vacuum chamber. The pressure was controlled by varying the Ar-flow rate and by adjusting the valve between the vacuum chamber and the vacuum pump. At pressures P>200 Pa the plasma started to flicker and at P>300 Pa there was no plasma glow and no electrical power consumption.

The results are presented in Figs. 8a and 8b, where the "normalised plasma intensity", I, given by

$$I = V_{probe}/V_{probe,max} \qquad (4)$$

$V_{probe,max}$ = 18.3 V DC, being the maximum value of V_{probe} measured with the current set-up, is plotted against the normalised probe position, $\phi = R/R_o$, R being the shortest distance from the probe to the inner surface of the inner electrode and R_o = 125 mm being the radius of the inner surface of the inner electrode.

As can be seen from Figs. 8a and 8b no charge build-up was observed for the reference probe. For the regular probes, positive charge build-up of the probes was generally observed (I>0); only at the lowest pressure a negative charge build-up was observed for the outermost electrode. This corresponds to the observation through the inspection window that at this pressure a clear Faraday dark space was present at the inner electrode surface. At higher pressures, the Faraday dark space was less clearly distinguishable. Thus it appears that the extent of the Faraday dark space, ε_1, can be measured by the plasma sensor according to the present invention.

Turning to Fig. 8a it appears that at pressures P<32 Pa the normalised plasma intensity is fairly homogeneously distributed in the majority of the volume inside the inner electrode; only near the inner electrode a lower normalised plasma intensity is observed due to the Faraday dark space near the inner electrode. This agrees well with the fact that an apparently homogeneous plasma glow was observed inside the inner electrode at these pressures.

At higher pressures, see Fig. 8b, the conditions have changed; the plasma intensity is no longer homogeneously distributed, a higher normalised plasma intensity is observed near the inner electrode. Also, this trend corresponds well with visual observations of the plasma glow which becomes gradually weaker in the centre of the inner electrode at increasing pressure.

A measure of the "plasma extent" for a given experimental set-up is given by the radial distance, $\varepsilon = \varepsilon_2 - \varepsilon_1$, where $\varepsilon_1 < \varepsilon_2 \leq 1$. With the current plasma sensor however, it is difficult to define ε_2 and thus ε. This requires the choice of a reference value I_{ref} that defines the intensity value at position $\phi = \varepsilon_2$, the boundary of the passive dark space.

To investigate the influence of the applied electrode AC potential difference on the charge build-up distribution, a further experiment was conducted in which the pressure was held constant at 40 Pa and the applied electrode voltage was varied in the range 250 - 1000 V rms. Argon was being fed to the chamber at a flow rate of 30 sccm.

The result is presented in Fig. 9, where the normalised plasma intensity is plotted against ϕ. The figure shows that the plasma intensity level attains a maximum at 600 V (rms) and that the plasma becomes more homogeneous as the applied electrode voltage is increased.

A larger passive dark space ($I < I_{ref}$) is observed at low applied voltages and that the extent of said passive dark space decreases as the applied electrode voltage is in-

creased. This observation agrees well with the visual observations.

METHOD AND APPARATUS FOR GAS PLASMA TREATMENT WITH CONTROLLED EXTENT OF GAS PLASMA, AND USE THEREOF

CLAIMS

1. A method of controlling the extent of gas plasma, the method comprising:

(A) providing a gas zone (110), said gas zone comprising a gas having a pressure; said gas comprising at least one gas component allowing generation of a plasma;

(B) generating a plasma in said gas zone by supplying a potential difference between at least two electrodes (150); said at least two electrodes being configured to wholly or partly encompass said gas zone; and

(C) controlling the extent of said generated plasma by controlling at least one of: said gas, said pressure, said potential difference, and said configuration of said at least two electrodes.

2. The method according to claim 1 wherein said gas is controlled by controlling the type of said gas, its composition, and/or the amount of its components.

3. The method according to claim 1 or 2 wherein said gas zone contains a gas component or a gas composition selected from the group comprising:

inert gasses, including noble gasses, preferably He, Ar, Ne, Xe;

oxidizing gasses, preferably O_2, NO_2, N_2O, CO_2;

halogen gasses, preferably Cl_2, F_2;

and reducing gasses, preferably H_2 and NH_3;

mixtures of said noble gasses with said halogen gasses, said oxidizing gasses, or with said reducing gasses;

a mixture of said halogen gasses with said oxidizing gasses, or with said reducing gasses; and

plasma polymerisable substances, including monomers, preferably selected from the group consisting of aliphatic hydrocarbons, including C_1-C_{16} alkanes such ethane, hexane ; C_2-C_{16} alkenes such as hexene, 1-hexene, 3-methyl-1-hexene, dienes such as 1,4-hexadiene, butadiene), 1,4-hexadiene; C_2-C_{16} alkynes including hexyne, 1-hexyne; aromatic hydrocarbons, including styrene, benzene; substituted benzenes; aromatic monomers of styrene compounds; monomers of vinyl compounds, including vinylpyrrolidone; acrylate compounds including methylacrylate, acrylonitrile, glycidylmethacrylate, methacrylacid-anhydride, and acrylic acid chloride,

and mixtures of said polymerisable substances and said inert gasses, halogen gasses, oxidizing gasses and reducing gasses.

4. A method according to any one of claims 1-3 wherein said pressure is controlled by controlling at least one gas outlet (120) and/or at least one gas inlet (130) of said gas zone.

5. A method according to any one of claims 1-4 wherein said pressure is in the range including 10 to 200 Pa, preferably 20 to 100 Pa, more preferably 30 to 80 Pa, most preferably 40 to 70 Pa, and in particular about 50 Pa.

6. A method according to any one of claims 1-4 wherein said pressure is in the range including 0.1 to 50 Pa, preferably 1 to 30 Pa, more preferably 2 to 20 Pa, most preferably 5 to 10 Pa.

7. A method according to any one of claims 1-6 wherein said potential difference is in the range including 200 to 2000 V, preferably 400 to 1500 V, more preferably 600 to 1200 V, most preferably 600 to 1100 V, and in particular 600 to 1000 V.

8. A method according to any one of claims 1-6 wherein said potential difference is in the range including 200 to 2000 V, preferably 200 to 1200 V, preferably 300 to 800 V, more preferably 300 to 700 V, and most preferably 300 to 600 V.

9. A method according to any one of claims 1-8 wherein said potential difference and said gas zone are adapted to provide a plasma power density in the range including 0.01 to 100 W/l, preferably 0.1 to 10 W/l, more preferably 0.1 to 5 W/l, most preferably 0.1 W/l to 3 W/l, and in particular about 1 W/l.

10. A method according to any one of claims 1-9 wherein the configuration of said at least two electrodes com-

prises at least one of: mutual distance, individual shapes, and mutual orientation.

11. A method according to any one of claims 1-10 wherein said at least two electrodes are arranged inside said gas zone, and/or outside said gas zone, preferably in form of concentric electrodes, optionally one of said electrodes being in form of a grid.

12. The method according to any one of claims 1-11 wherein the extent of plasma is modified by introducing an additional electrical field, a magnetic field, and/or a shield.

13. The method according to claim 12 wherein said shield is selected from the group comprising absorbers, reflectors, deflectors and masks.

14. The method according to claim 13 wherein said absorbers, reflectors, deflectors or masks comprise a material selected from the group comprising metallic, preferably stainless steel; non-metallic, preferably glass; and insulating materials, preferably glass, ceramic, and a polymeric material, including rubber, and thermoplastic materials, preferably polyethylene(PE), Polypropylene(PP), polyvinylchloride (PVC), polyamide (PA), polyvinyldifluoride (PVDF), and carbon-filled polyethylene; other polymer materials, including non-thermoplastic polymers, preferably polyesters; and combinations thereof.

15. A method according to any one of claims 1-14 wherein said extent of plasma is adapted so that at least one

object arranged in said gas is exposed, or not exposed, wholly or partly to said plasma.

16. A method according to claim 14 wherein said at least one object comprises: a substrate; a substrate holder; a sensor, preferably a deposition monitoring sensor, or a plasma intensity sensor; and a sputtering electrode.

17. The method according to claim 16 wherein the position of said substrate, said substrate holder, said sensor holder with respect to one of said at least two electrodes is so that the normalized substrate position ϕ is in the range including 0.3 to 1, preferably including 0.5 to 1, in particular including 0.9 to 1.

18. A method according to any one of claims 1-17 wherein said extent of plasma in said gas zone is determined by direct measurement.

19. A method according to any one of claims 1-18 wherein said extent of plasma in said gas zone is determined by a priori calibration.

20. A method according to any one of claims 1-19 wherein said voltage difference being generated by power supply comprising: a direct current (DC) power supply, an alternating current (AC) power supply: at sub-radio frequencies, including main frequencies (50-60 Hz), low frequencies (LF), and audio frequencies (AF); at radio frequencies (RF), and at microwave frequencies (MW).

21. A plasma treatment apparatus with controlled extent of gas plasma, the apparatus comprising:

(A) a gas section (110), said gas section comprising at least one gas inlet and at least one gas outlet adapted for providing a gas having a pressure;

(B) at least two electrodes (150), said at least two electrodes being configured to wholly or partly encompass said gas section;

(C) at least one power supply (155), said at least one power supply supplying a potential difference between at least two of said at least two electrodes for generating a plasma in said gas section;

(D) at least one plasma measuring means (160) for measuring the extent of the plasma in said gas section with respect to at least one of said at least two electrodes; and

(E) at least one controlling means (180,191,131) for controlling the extent of said generated plasma; said at least one controlling means being adapted to control at least one of: said gas, said pressure, said potential difference, and said configuration of said at least two electrodes in response to a measurement of said at least one plasma measuring means.

22. The apparatus according to claim 21 wherein said at least one controlling means comprises means for controlling the type of said gas, its composition, and/or the amount of its components.

23. The apparatus according to claim 21 or 22 wherein said gas section contains a gas component or a gas composition selected from the group comprising:

inert gasses, including noble gasses, preferably He, Ar, Ne, Xe;

oxidizing gasses, preferably O_2, NO_2, N_2O, CO_2;

halogen gasses, preferably Cl_2, F_2;

and reducing gasses, preferably H_2 and NH_3;

mixtures of said noble gasses with said halogen gasses, said oxidizing gasses, or with said reducing gasses;

a mixture of said halogen gasses with said oxidizing gasses, or with said reducing gasses; and

plasma polymerisable substances, including monomers, preferably selected from the group consisting of aliphatic hydrocarbons, including C_1-C_{16} alkanes such ethane, hexane ; C_2-C_{16} alkenes such as hexene, 1-hexene, 3-methyl-1-hexene, dienes such as 1,4-hexadiene, butadiene), 1,4-hexadiene; C_2-C_{16} alkynes including hexyne, 1-hexyne; aromatic hydrocarbons, including styrene, benzene; substituted benzenes; aromatic monomers of styrene compounds; monomers of vinyl compounds, including vinylpyrrolidone; acrylate compounds including methylacrylate, acrylonitrile, glycidylmethacrylate, methacrylacid-anhydride, and acrylic acid chloride,

and mixtures of said polymerisable substances and said inert gasses, halogen gasses, oxidizing gasses and reducing gasses.

24. An apparatus according to any one of claims 21-23 wherein said at least one controlling means comprises means for controlling at least one gas outlet (120), preferably a reduction valve (122) controlled by a pressure controller (191) and a pressure transducer (190), and/or means to control at least one gas inlet (130), preferably a flow controller (131), said means for controlling said gas outlet and said gas inlet preferably being controlled by a computer (180).

25. An apparatus according to any one of claims 21-24 wherein said pressure is in the range including 10 to 200 Pa, preferably 20 to 100 Pa, more preferably 30 to 80 Pa, most preferably 40 to 70 Pa, and in particular about 50 Pa.

26. An apparatus according to any one of claims 21-24 wherein said pressure is in the range including 0.1 to 50 Pa, preferably 1 to 30 Pa, more preferably 2 to 20 Pa, most preferably 5 to 10 Pa. 27. An apparatus according to any one of claims 21-26 wherein said at least one power supply comprises: a direct current (DC) power supply, an alternating current (AC) power supply which at sub-radio frequencies, include a mains frequency (50-60 Hz) power supply, a low frequency (LF) power supply, and an audio frequency (AF) power supply; and which at higher frequencies include a radio frequency (RF) power supply, and a microwave frequency (MW) power supply.

28. An apparatus according to any one of claims 21-27 wherein said at least one controlling means comprises means for controlling said potential difference in the range including 200 to 2000 V, preferably 400 to 1500 V, more preferably 600 to 1200 V, most preferably 600 to 1100 V, and in particular 600 to 1000 V.

29. An apparatus according to any one of claims 21-27, wherein said at least one controlling means comprises means for controlling said potential difference in the range including 200 to 2000 V, preferably 200 to 1200 V, preferably 300 to 800 V, more preferably 300 to 700 v, and most preferably 300 to 600 V.

30. An apparatus according to any one of claims 21-29 wherein said potential difference and said gas section are adapted to provide a plasma power density in the range including 0.01 to 100 W/l, preferably 0.1 to 10 W/l, more preferably 0.1 to 5 W/l, most preferably 0.1 W/l to 3 W/l, and in particular about 1 W/l.

31. An apparatus according to any one of claims 21-30 wherein said at least one controlling means comprises configuration means for controlling the configuration of said at least two electrodes, said configuration means comprising distance-adjusting means for adjusting the mutual distance, preferably a telescopic expander, and/or a displaceable electrode carrier; shaping means for shaping an electrode, preferably a remotely deformable electrode, and/or a pre-shaped electrode; and orientation means for adjusting mutual orientation, preferably a rotational electrode carrier.

32. An apparatus according to any one of claims 21-31 wherein said at least two electrodes are arranged inside said gas section, and/or outside said gas section.

33. The apparatus according to any one of claims 21-32 wherein said electrodes are made of an electrically conductive material which is resistant to oxide formation and sputtering, preferably stainless steel.

34. The apparatus according to any one of claim 21-33 wherein said at least two electrodes comprise a circumferential electrode, preferably at least two concentric ellipsoidal electrodes.

35. The apparatus according to claim 34 wherein one of said circumferential electrodes comprise a grid electrode, preferably the inner electrode being a grid electrode, more preferably a grid electrode having a grid size in the range including 5 to 50 mm, preferably 5 to 20 mm, more preferably about 10 mm.

36. The apparatus according to any one of claims 21-35 wherein said at least one plasma measuring means comprises inspection means for optical inspection.

37. The apparatus according to claim 36 wherein said optical inspection means comprises means for visual inspection, preferably said visual inspection means comprises an inspection window, and a telescope.

38. The apparatus according to claims 36 or 37 wherein said inspection means comprises a plasma sensor, or a set of plasma sensors, preferably an optical sensor; or an

electrical sensor, in particular an electrical sensor comprising a voltage probe and a voltmeter.

39. An apparatus according to any one of claims 21-38 wherein said at least one controlling means comprises: electrical field-generating means for generating an additional electrical field, preferably at least two electrodes positioned internally and/or externally to said gas section; magnetic field-generating means for generating a magnetic field, preferably at least one magnet, or inductive coil, positioned internally and/or externally to said gas section; and/or shielding means for wholly or partly shielding objects not to be exposed to plasma.

40. The apparatus according to claim 39 wherein said shielding means is selected from the group comprising absorbers, reflectors, deflectors, and masks.

41. The apparatus according to claim 39 or 40 wherein said shielding means comprise a material selected from the group comprising metallic, preferably stainless steel; non-metallic, preferably glass; and insulating materials, preferably glass, ceramic, and polymeric materials, including rubber, thermoplastic material, thermosetting materials, preferably polyethylene(PE), Polypropylene(PP), polyvinylchloride (PVC), polyamide (PA), polyvinyldifluoride (PVDF), carbon-filled polyethylene, polyesters, and combinations thereof.

42. An apparatus according to any one of claims 21-41 wherein said at least one controlling means comprises means for arranging at least one object in said gas sec-

tion so that said at least one object is exposed, or not exposed, wholly or partly to said plasma.

43. The apparatus according to claim 42 wherein said at least one object comprises: a substrate; a substrate holder; a sensor, preferably a deposition monitoring sensor, or a plasma intensity sensor; and a sputtering electrode.

44. The apparatus according to claim 43 wherein the position of said substrate with respect to one of said at least two electrodes is so that the normalized substrate position ϕ is in the range including 0.3 to 1, preferably including 0.5 to 1, in particular including 0.9 to 1.

45. The apparatus according to any one of claims 21-44 further comprising a sluice for introducing into or for removing from the gas section at least one substrate.

46. The apparatus according to claim 45 wherein said sluice comprises an entrance sluice section, said entrance sluice section comprising a first product valve for introducing said substrate holder and/or at least one substrates therein; and a second product valve for introducing said substrate holder and/or at least one substrate into said reaction section; a gas outlet for evacuating said entrance sluice section; and a gas inlet.

47. The apparatus according to claims 45 or 46 wherein said sluice comprises an exit sluice section, said exit sluice section comprising a first product valve for removing said substrate holder and/or at least one substrate from said gas section; and a second product valve

for removing said substrate holder and/or at least one substrate from said exit sluice section; a gas outlet for evacuating said exit sluice section; and a gas inlet.

48. Use of a method of controlling the extent of plasma as defined in claims 1-20 in a method comprising plasma treatments and/or plasma-assisted surface modification of electrodes and/or substrates, preferably including plasma cleaning, plasma etching, plasma activation, and plasma deposition of electrodes, substrates, or both.

49. Use of a plasma treatment apparatus as defined in claims 21-47 in a method comprising in plasma treatments and/or plasma-assisted surface modification of electrodes and/or substrates, preferably including plasma cleaning, plasma etching, plasma activation, and plasma deposition of electrodes, substrates, or both.

50. Use according to claims 48 or 49 wherein plasma deposition comprises plasma polymerisation, and/or metallization.

51. Use according to claims 48 or 49 wherein plasma activation comprises radical formation, and/or oxidation, or reduction.

52. A method of plasma electrode cleaning, the method comprising controlling the extent of a plasma according to a method as defined in claims 1-20, and/or using an apparatus as defined in claims 21-47 wherein said extent of plasma in said gas zone and/or in said gas section does not contact a substrate, or a part thereof, and wherein said gas zone and/or said gas section contains a cleaning gas.

53. A method of plasma deposition, the method comprising controlling the extent according to a method as defined in claims 1-20, and/or using an apparatus as defined in claims 21-47 wherein said extent of plasma in said gas zone and/or in said gas section extends to contact with a substrate, or a part thereof, and wherein said gas zone and/or said gas section contains a substance to be plasma deposited on said substrate.

54. A method of preparing a substrate by plasma treatment, the method comprising:

(a) optional pre-cleaning the substrate by wet chemical cleaning;

(b) introducing said optionally pre-cleaned substrate into the reaction section of a plasma deposition apparatus comprising at least two electrodes as defined in claims 21, 32-35;

(c) plasma cleaning said at least two electrodes by controlling the extent of plasma according to a method as defined in claims 1-20 wherein said extent of plasma in said gas zone and/or in said gas section does not extends to contact with the substrate, or a part thereof;

(d) optionally pre-treating the substrate by an inert gas plasma;

(e) optionally pre-treating the substrate by a reducing gas plasma;

(f) optionally treating the optionally pre-treated substrate by a base coat deposition gas plasma; and

(g) treating the optionally base-coat treated substrate by a top coat deposition gas plasma;

wherein said treatments (c)-(g) comprise controlling the extent of plasma according to a method as defined in claims 1-20 wherein said extent of plasma in said gas zone and/or in said gas section extends to contact with the substrate, or a part thereof.

55. A method according to claim 54 wherein the pressure is reduced to increase in extent of plasma to contact with the substrate for said treatments (c)-(g).

56. A method according to claims 54 and 55 wherein said inert gas comprises argon; said reducing gas comprises hydrogen; said base coating deposition gas plasma comprises hexene; and said top coat deposition gas plasma comprises an acid halide, preferably acrylic acid chloride, or acrylonitrile.

57. A method according to any one of claims 54-56 wherein said substrate comprises a material selected from the group comprising glass; silicon; metal, preferably stainless steel, platinum; polymer, preferably polystyrene, polypropylene, and rubber, preferably silicone rubber.

58. A method according to any one of claims 54-57 wherein said substrate is in form of a microscope slide for bio assays.

59. A plasma treatment apparatus, the apparatus comprising:

(A) a gas section (110), said gas section comprising at least one gas inlet and at least one gas outlet for providing a gas at a given pressure;

(B) at least two electrodes (150), said at least two electrodes being configured to wholly or partly encompass said gas section;

(C) at least one power supply (155), said at least one power supply supplying a potential difference between at least two of said at least two electrodes for providing a plasma in said gas;

(D) a sluice (211,216;212,217) for introducing and/or removing a least one substrate into and/or from said gas section.

60. The apparatus according to claim 59 wherein said sluice comprises an entrance sluice section, said entrance sluice section comprising a first product valve for introducing said substrate holder and/or at least one substrates therein; and a second product valve for introducing said substrate holder and/or at least one substrate into said gas section; a gas outlet for evacuating said entrance sluice section; and a gas inlet.

61. The apparatus according to claims 59 or 60 wherein said sluice comprises an exit sluice section, said exit sluice section comprising a first product valve for removing said substrate holder and/or at least one substrate from said gas section; and a second product valve

for removing said substrate holder and/or at least one substrate from said exit sluice section; a gas outlet for evacuating said exit sluice section; and a gas inlet.

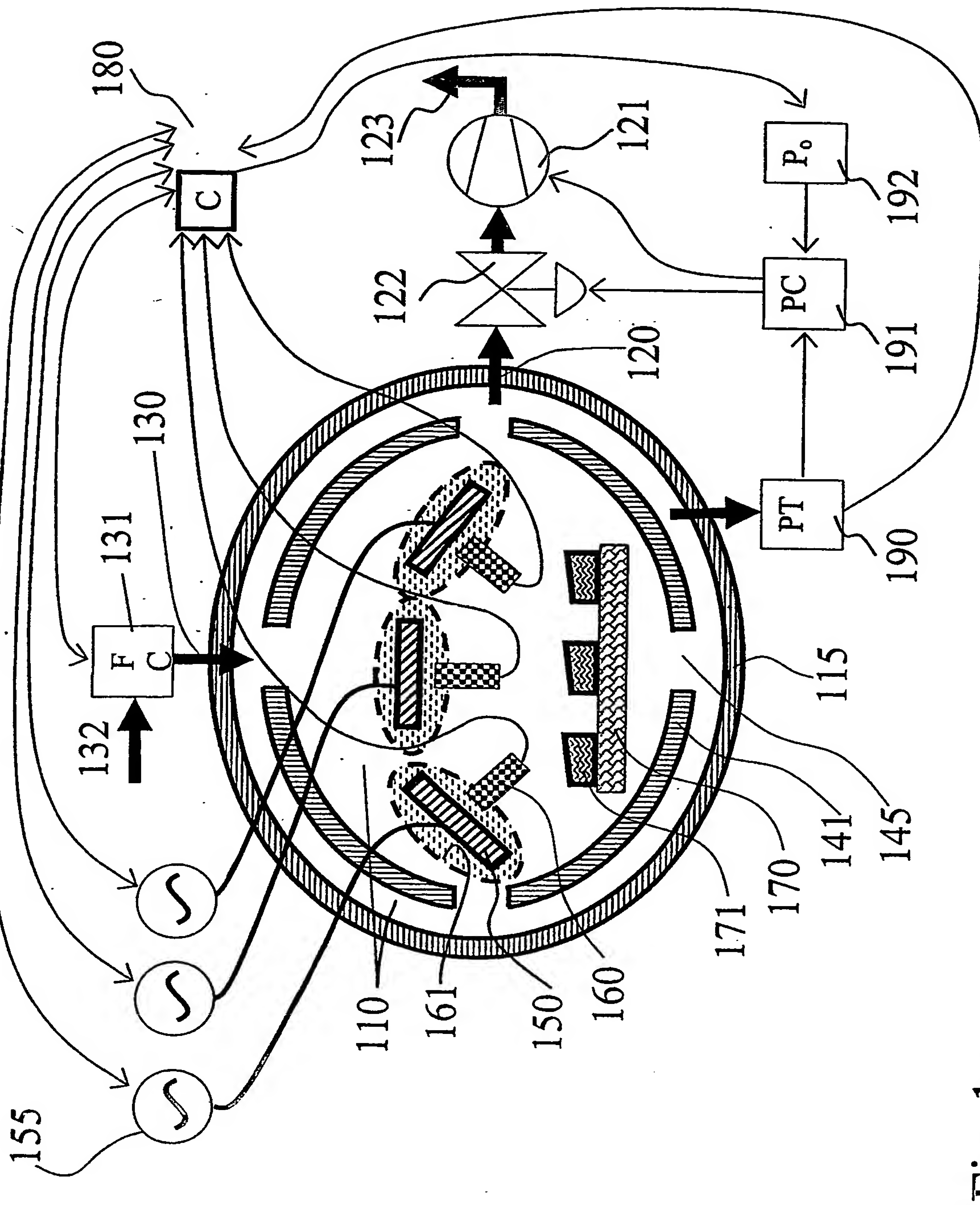

180
C
123
121
P0
192
122
PC
191
120
130
131
F C
132
PT
190
115
145
141
170
171
160
150
161
110
155

Fig. 1a

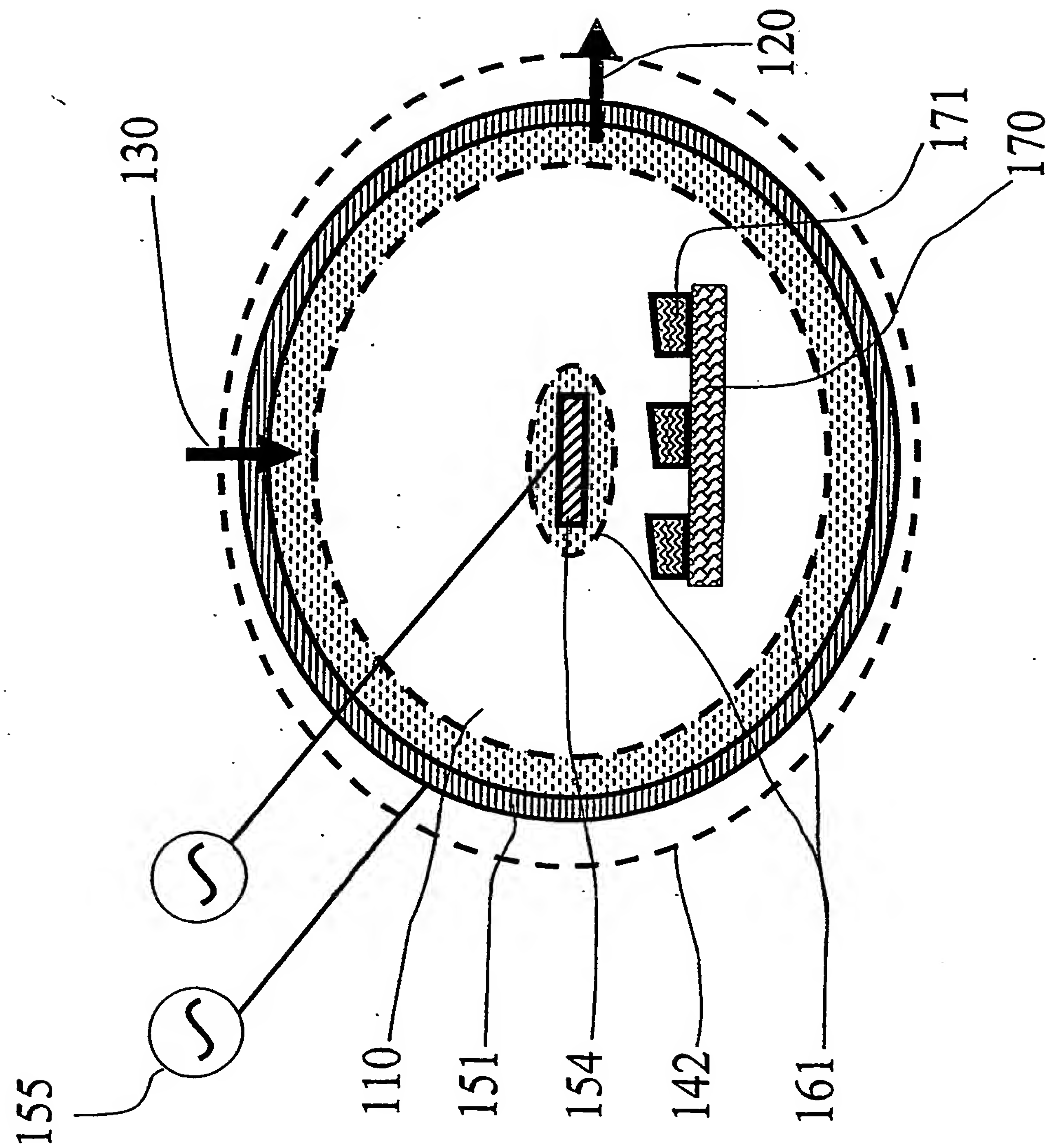
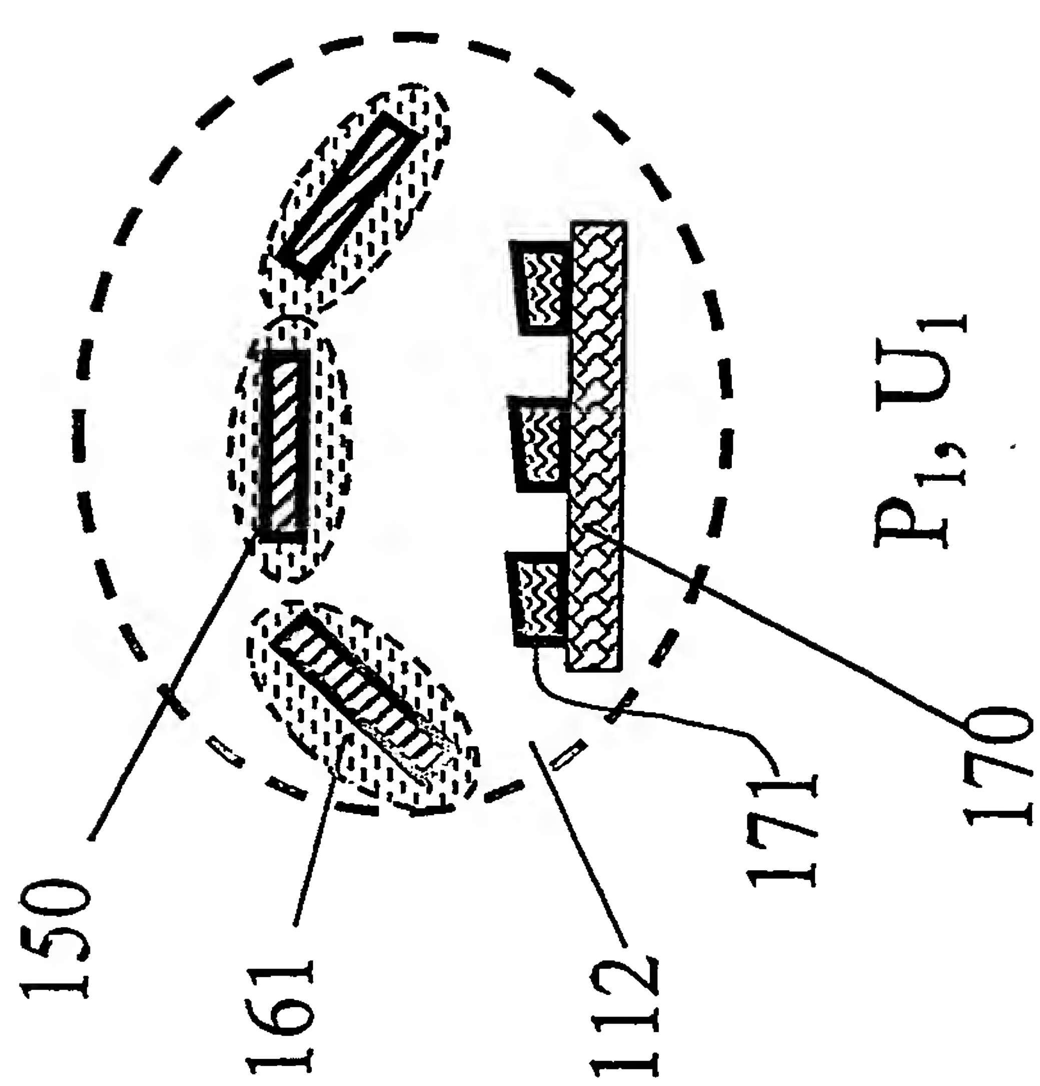
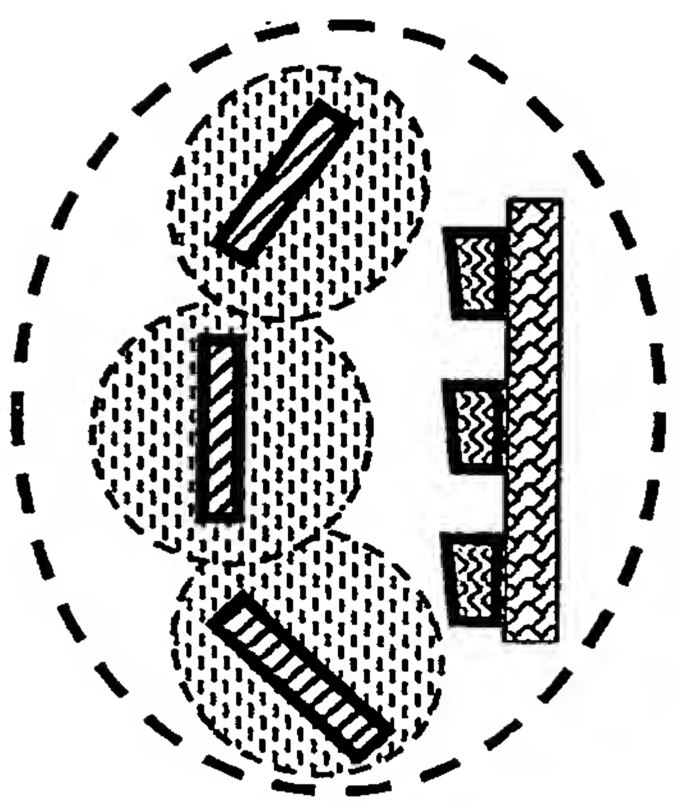


Fig. 1b



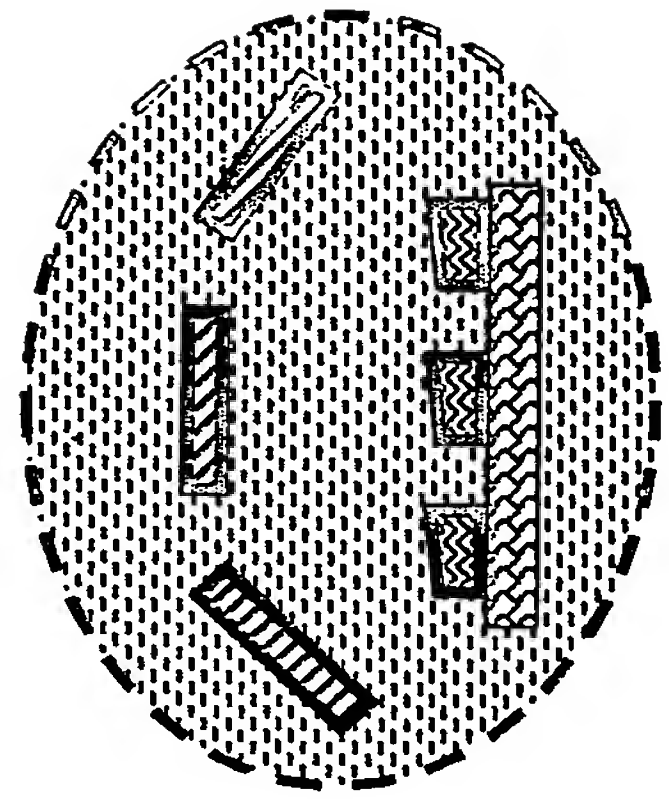
P_1, U_1

Fig. 1c



P_2, U_2

Fig. 1d



P_3, U_3

Fig. 1e

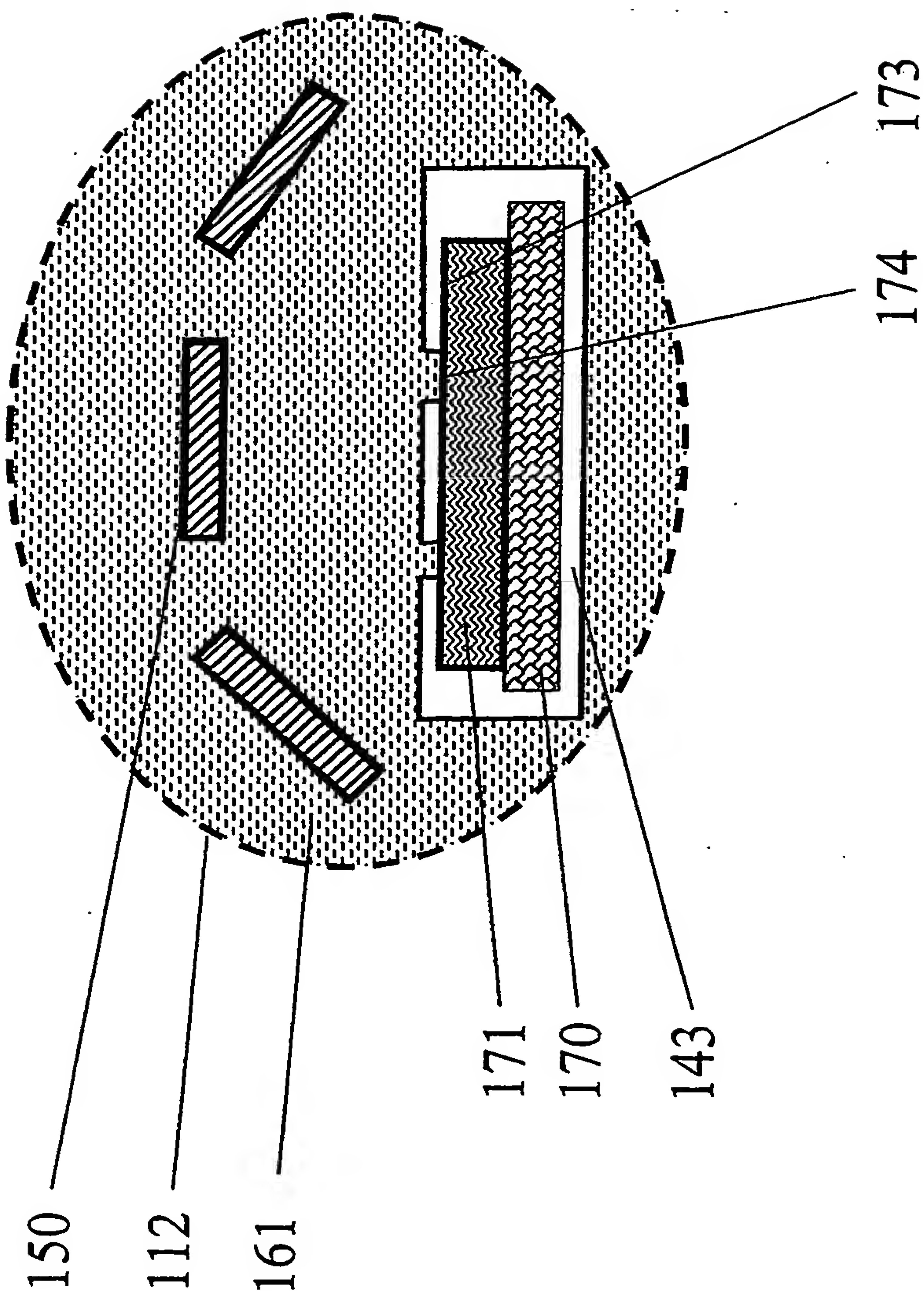


Fig. 1f

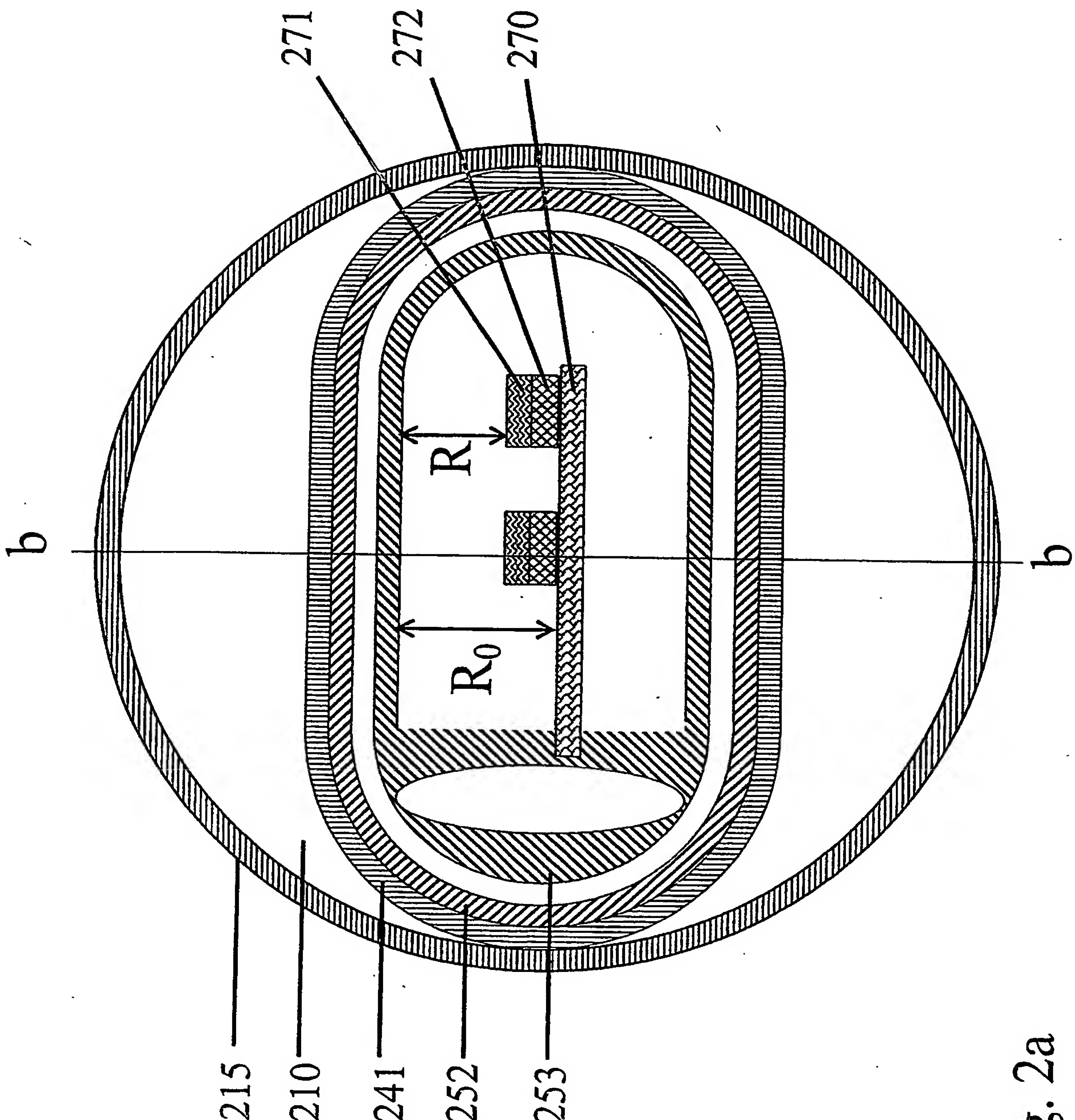


Fig. 2a

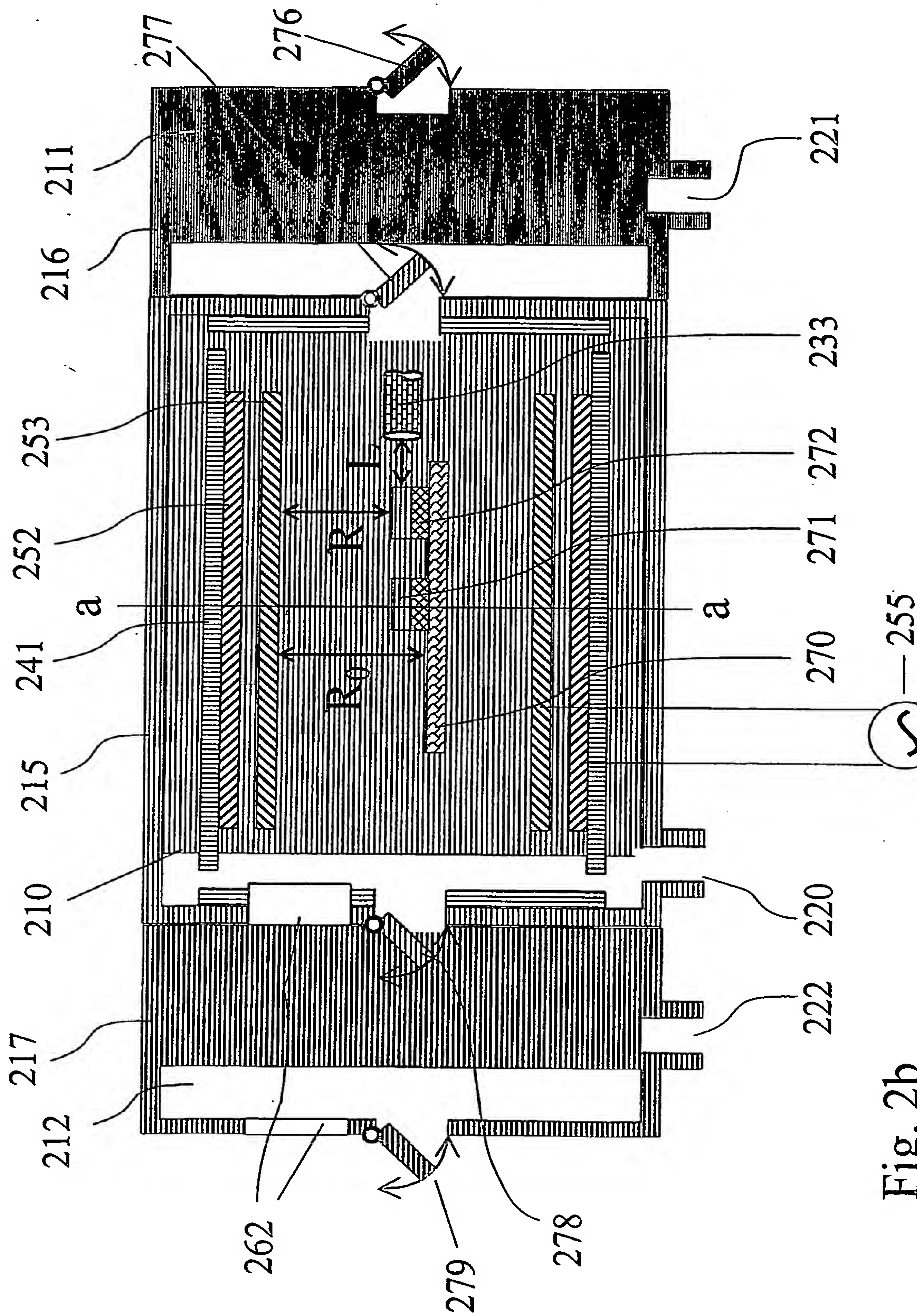
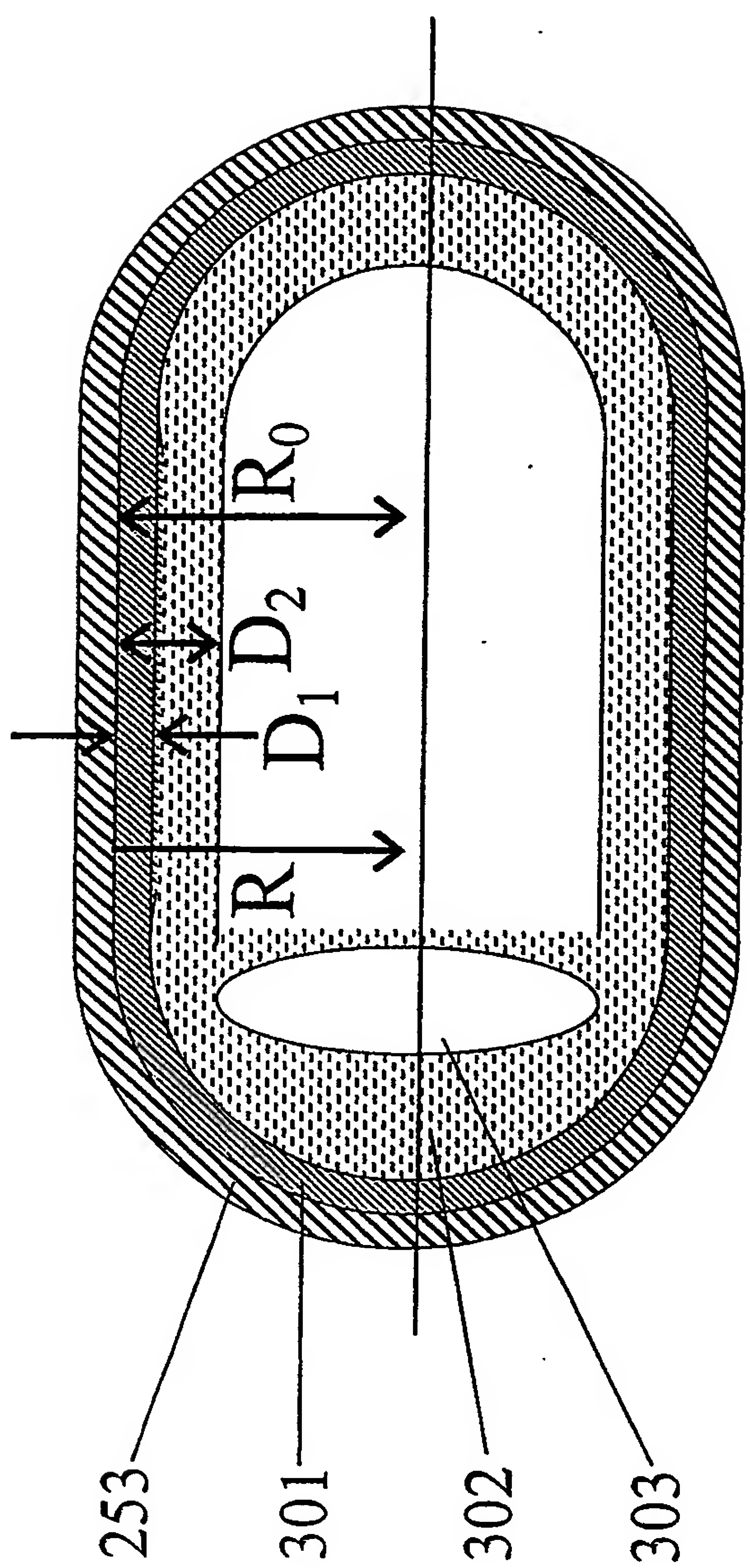

277
276
211
221
216
233
253
272
252
R
L
271
a
a
241
255
270
R_0
215
210
220
217
222
212
262
278
279

Fig. 2b



$$\phi = R/R_0$$

$$\varepsilon_i = D_i/R_0\,,\ i = 1, 2$$

$$\varepsilon = \varepsilon_2 - \varepsilon_1$$

Fig. 3

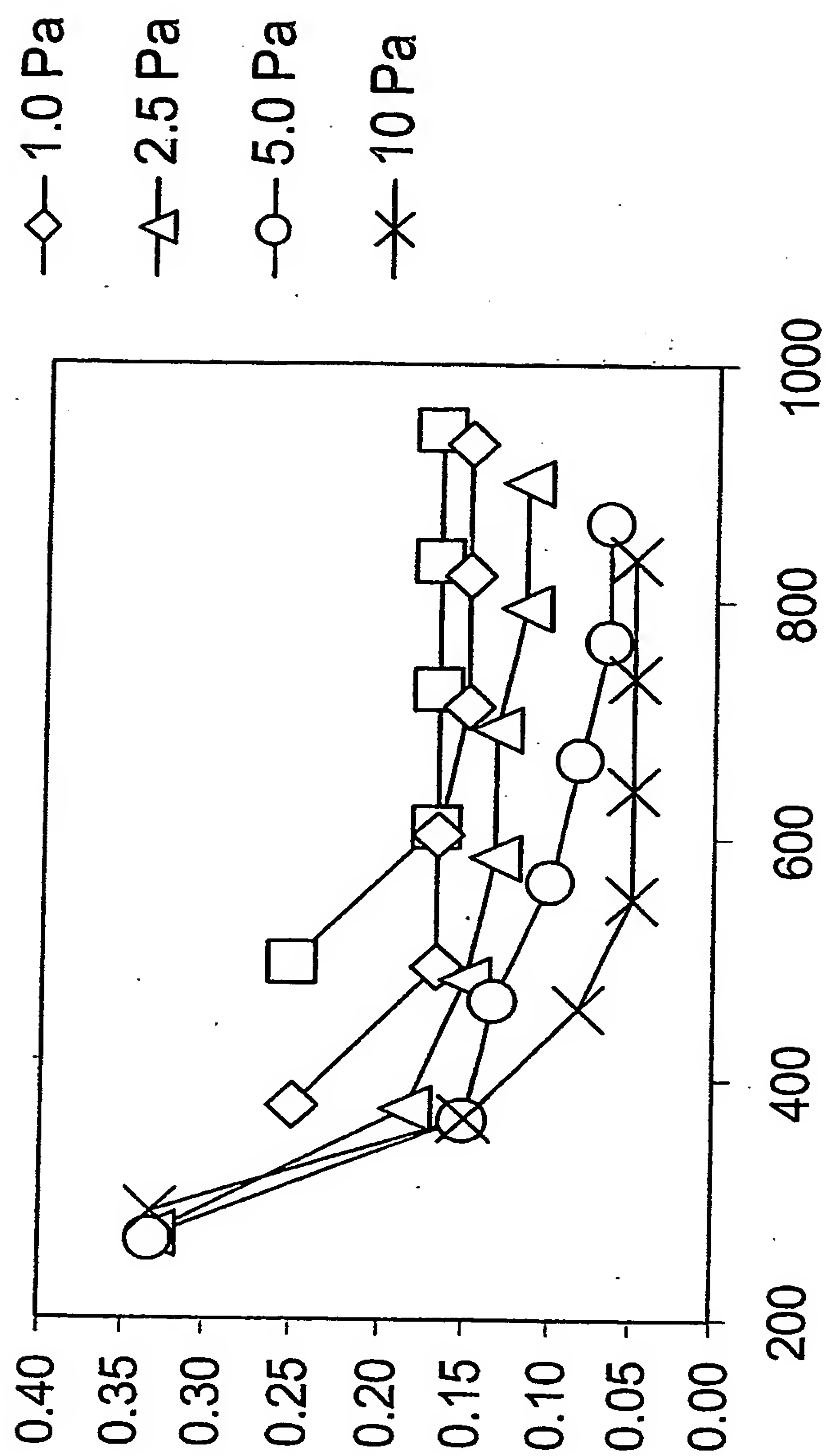

0.5 Pa
1.0 Pa
2.5 Pa
5.0 Pa
10 Pa
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
200
400
600
800
1000

Fig. 4a

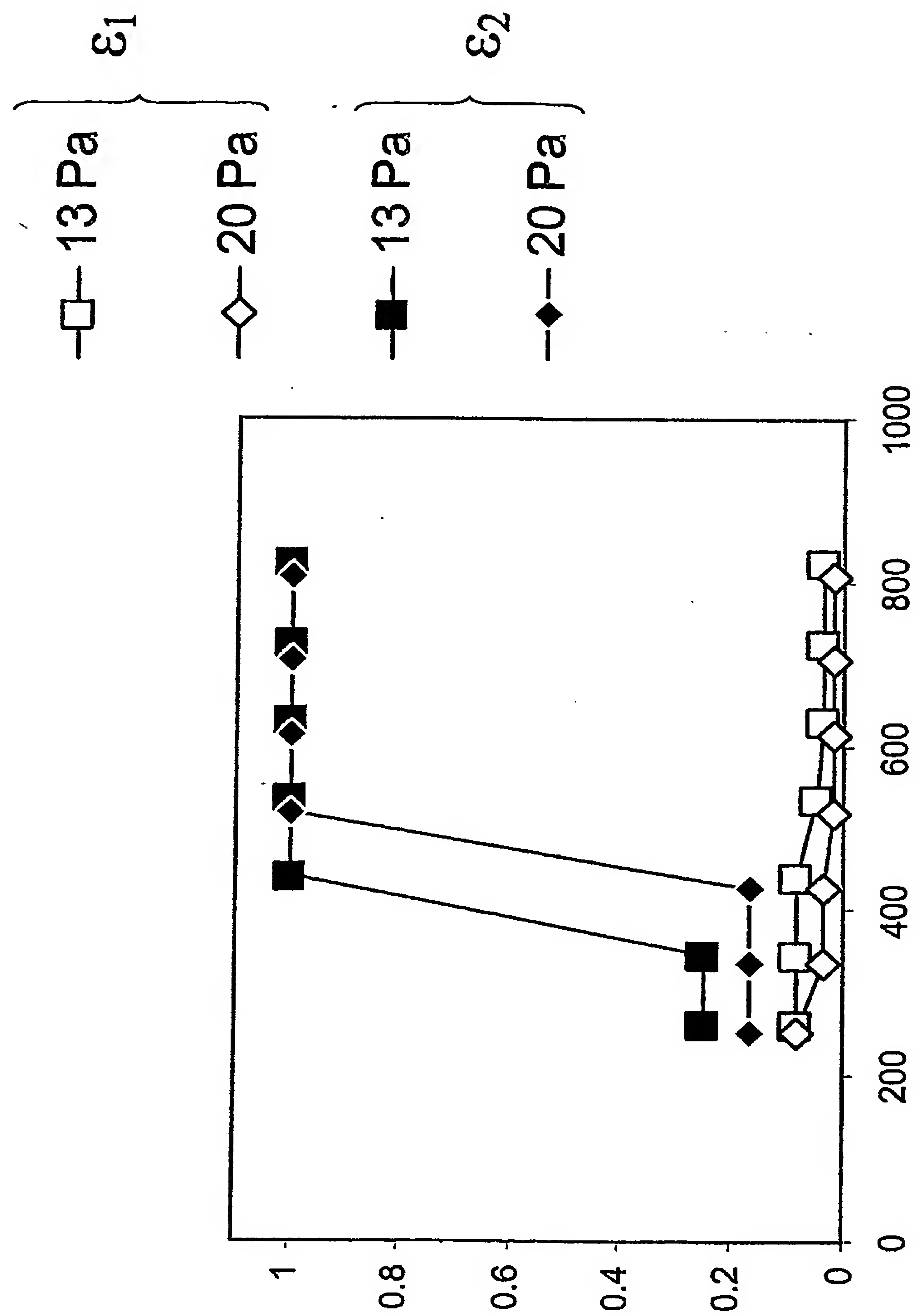

13 Pa
20 Pa
ε_1
13 Pa
20 Pa
ε_2
0
0.2
0.4
0.6
0.8
1
0
200
400
600
800
1000

Fig. 4b

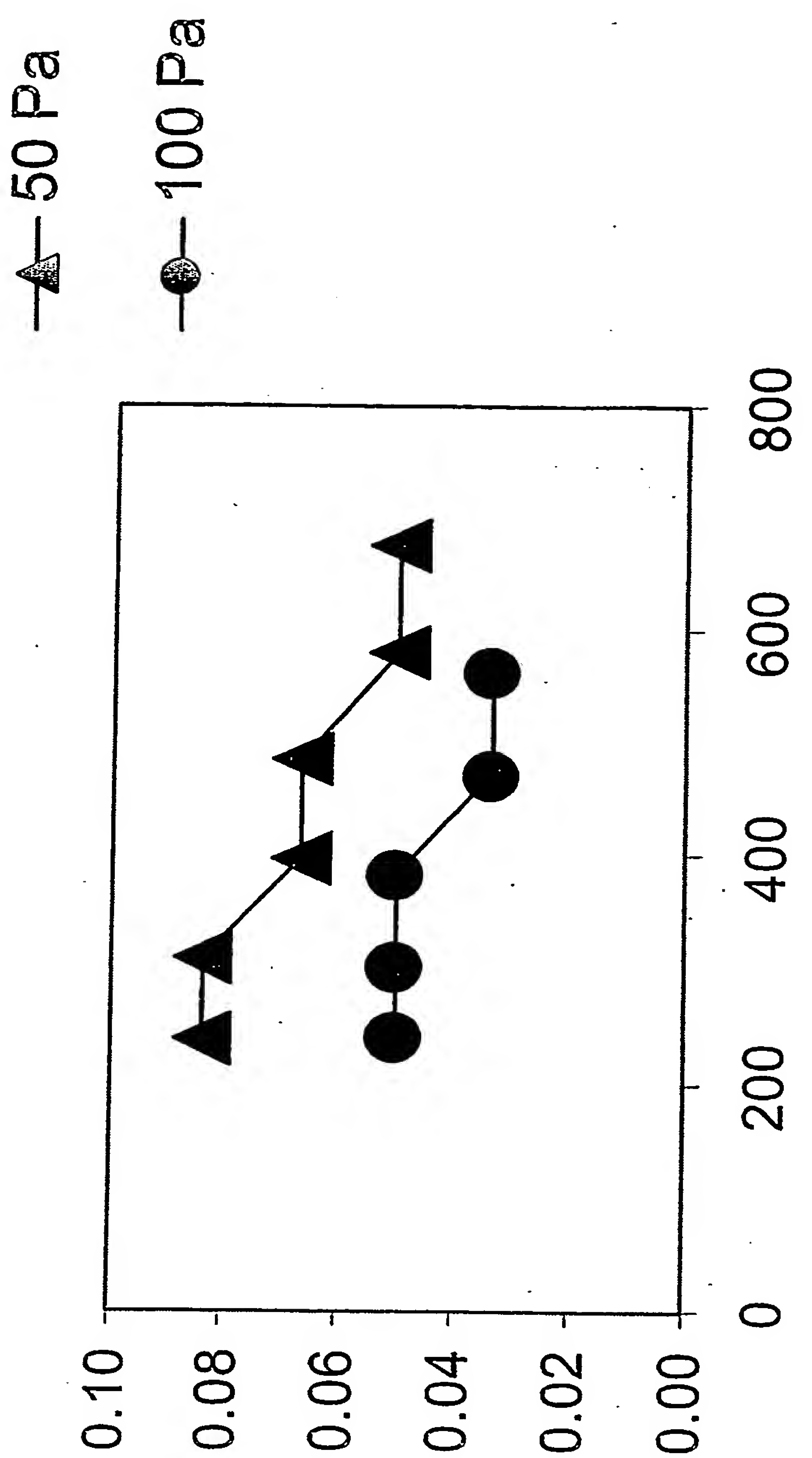


Fig. 4c

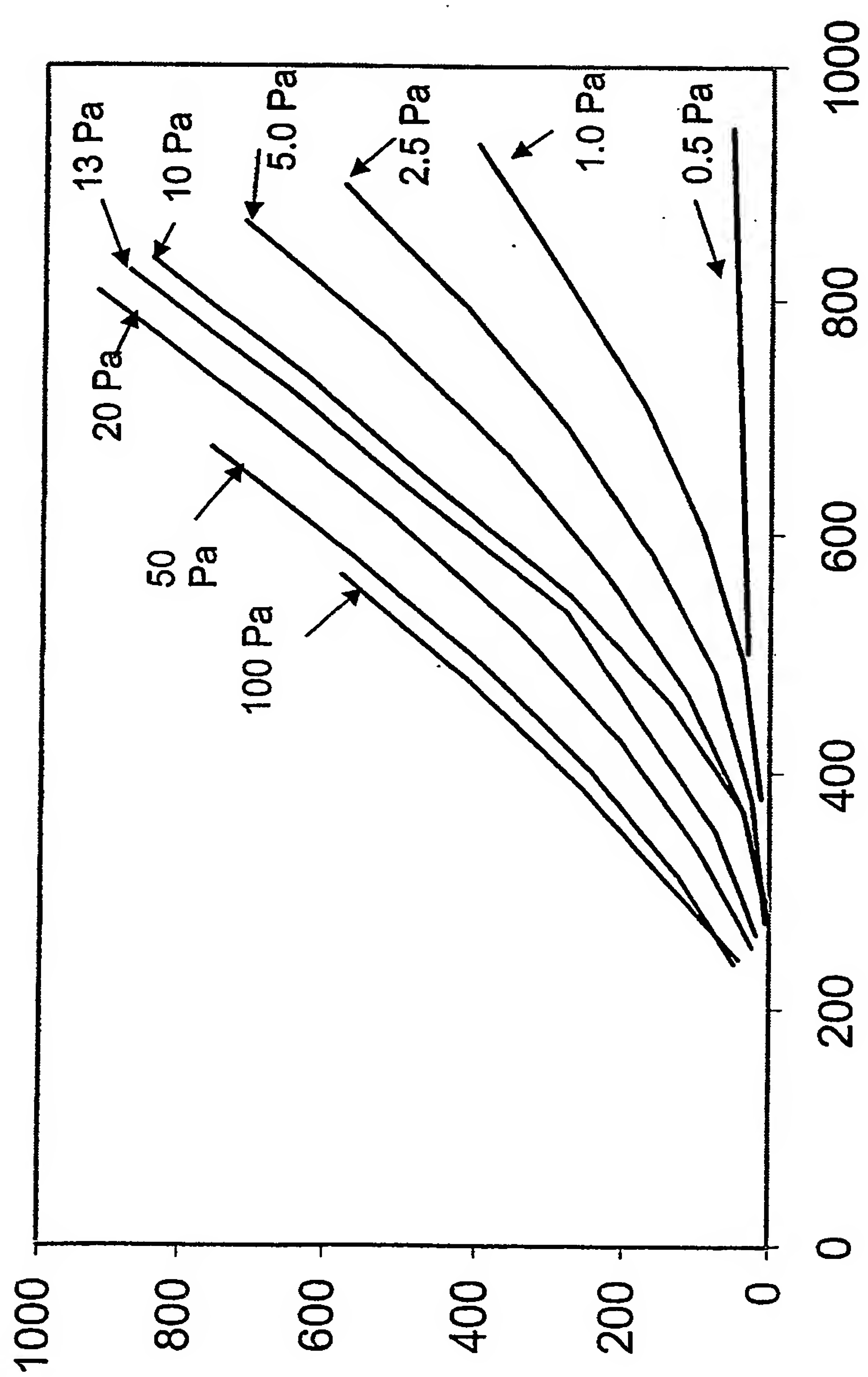

13 Pa
10 Pa
5.0 Pa
2.5 Pa
1.0 Pa
0.5 Pa
20 Pa
50 Pa
100 Pa
0
200
400
600
800
1000

Fig. 4d

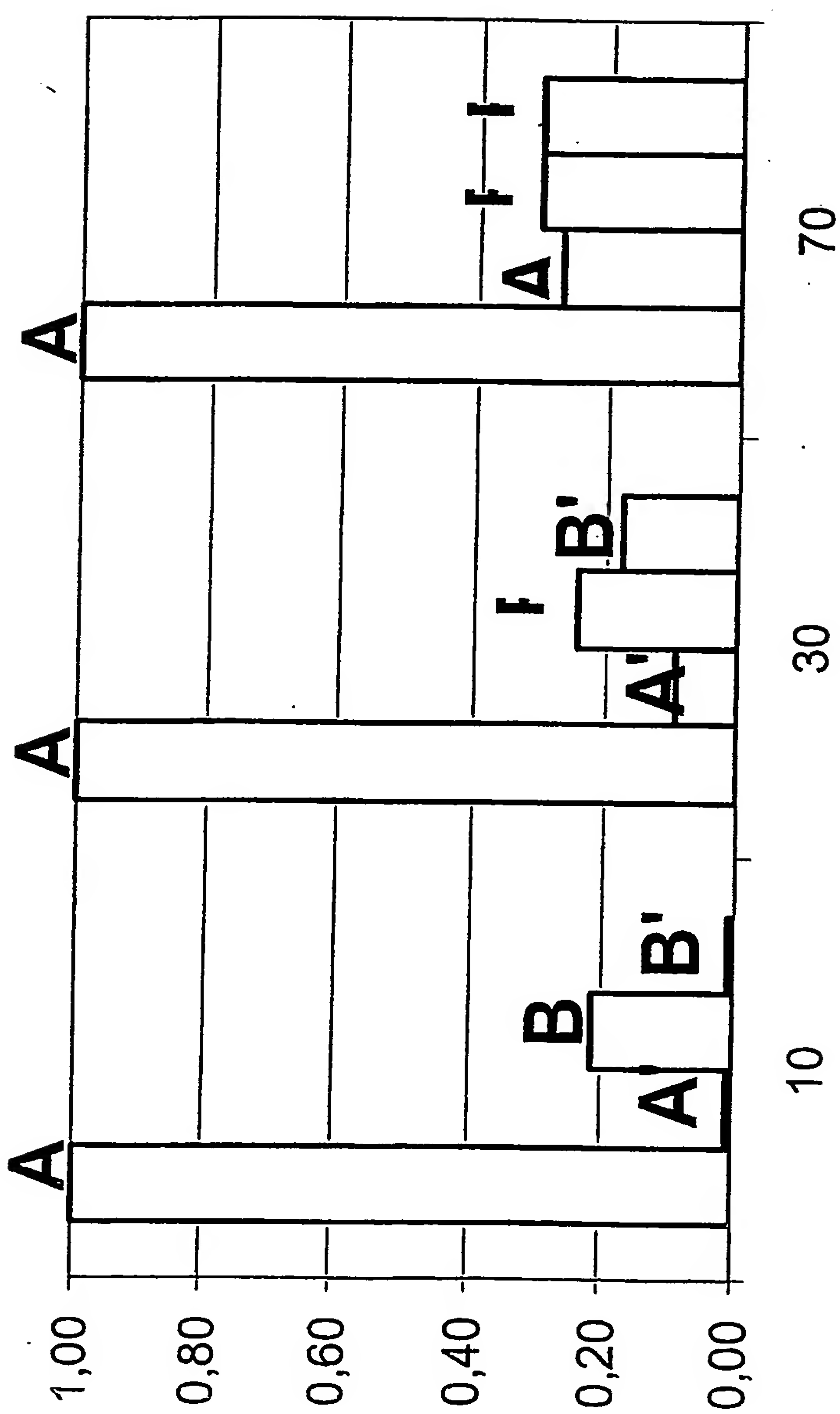


Fig. 5a.

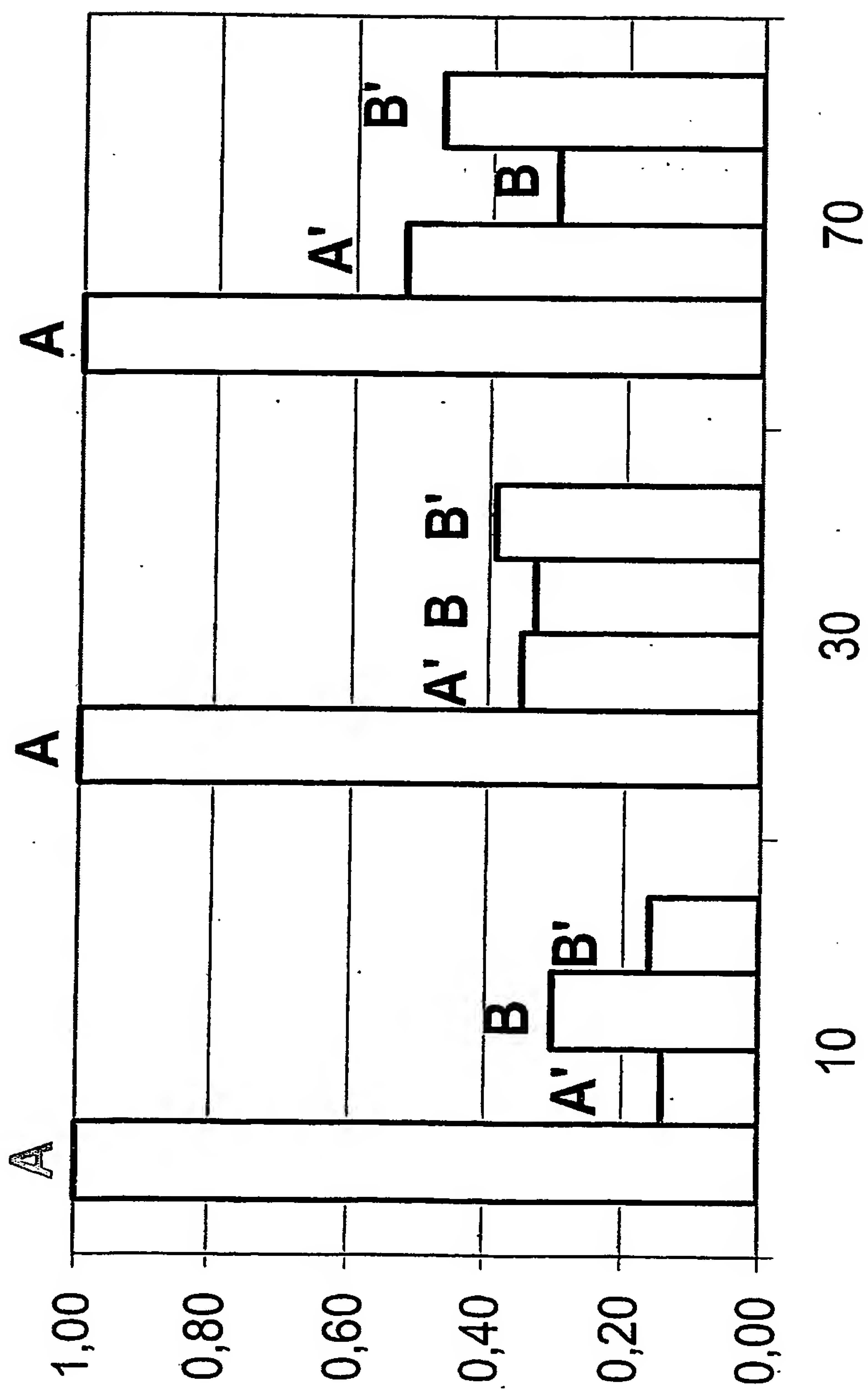


Fig. 5b.

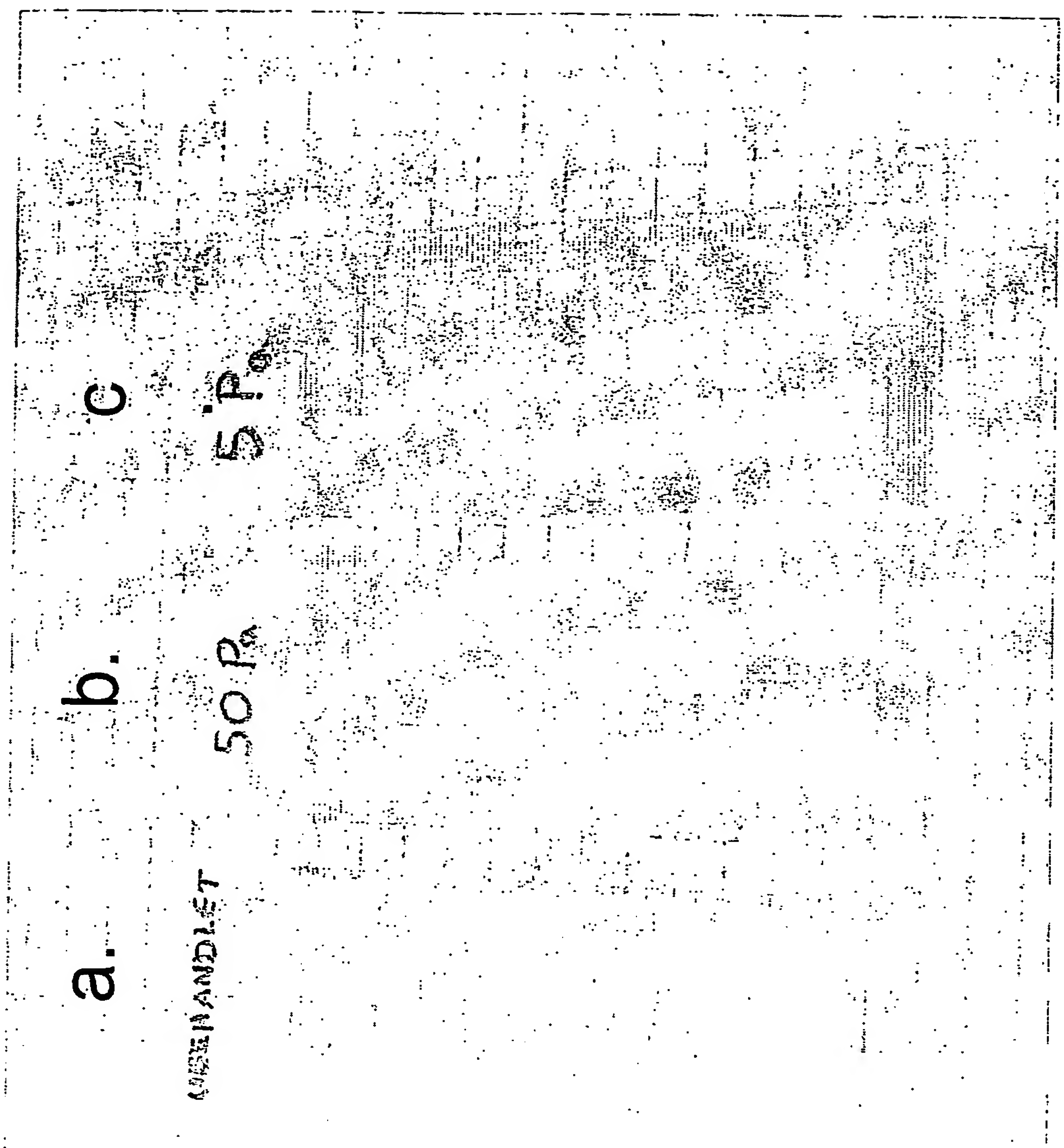


Fig. 6

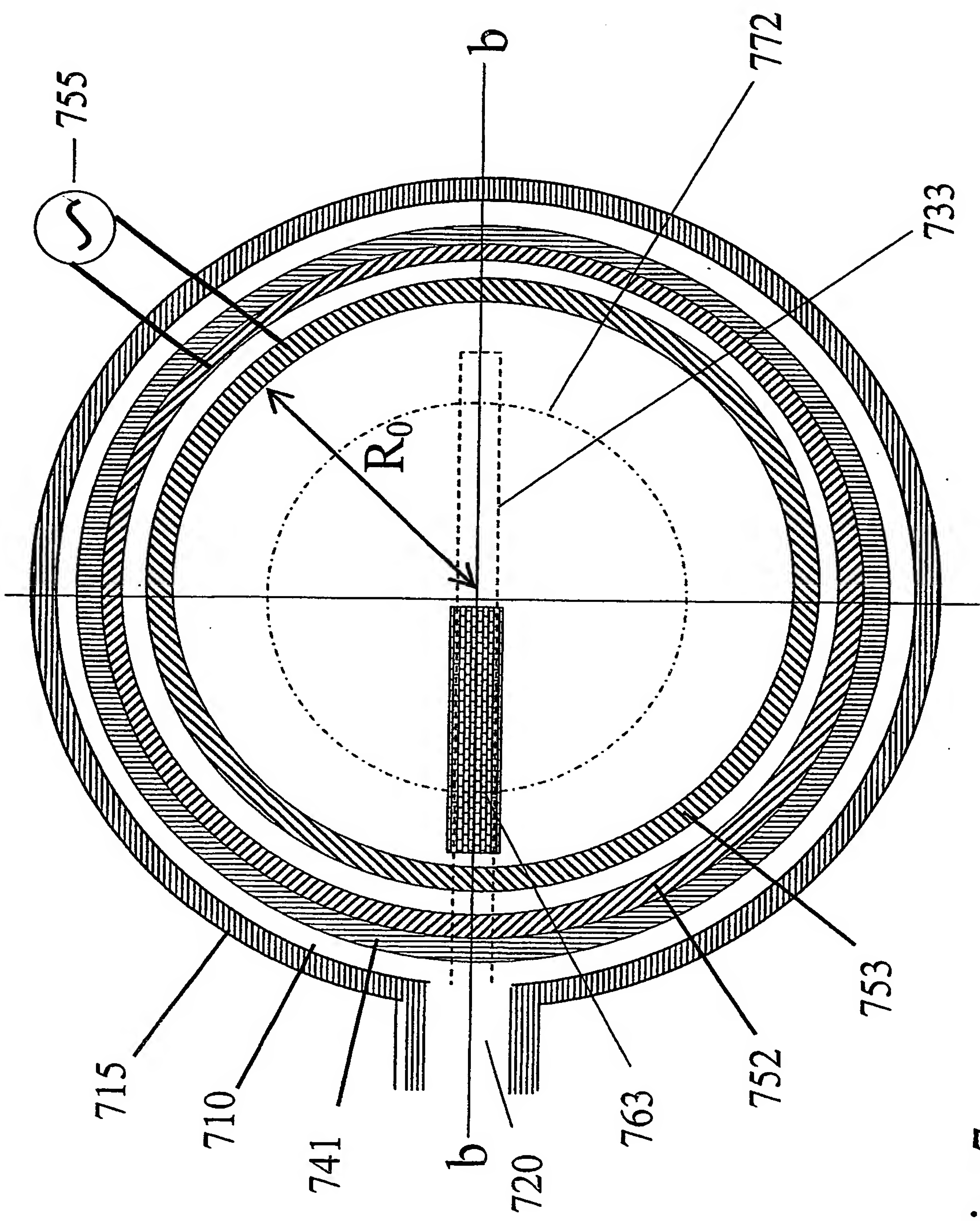
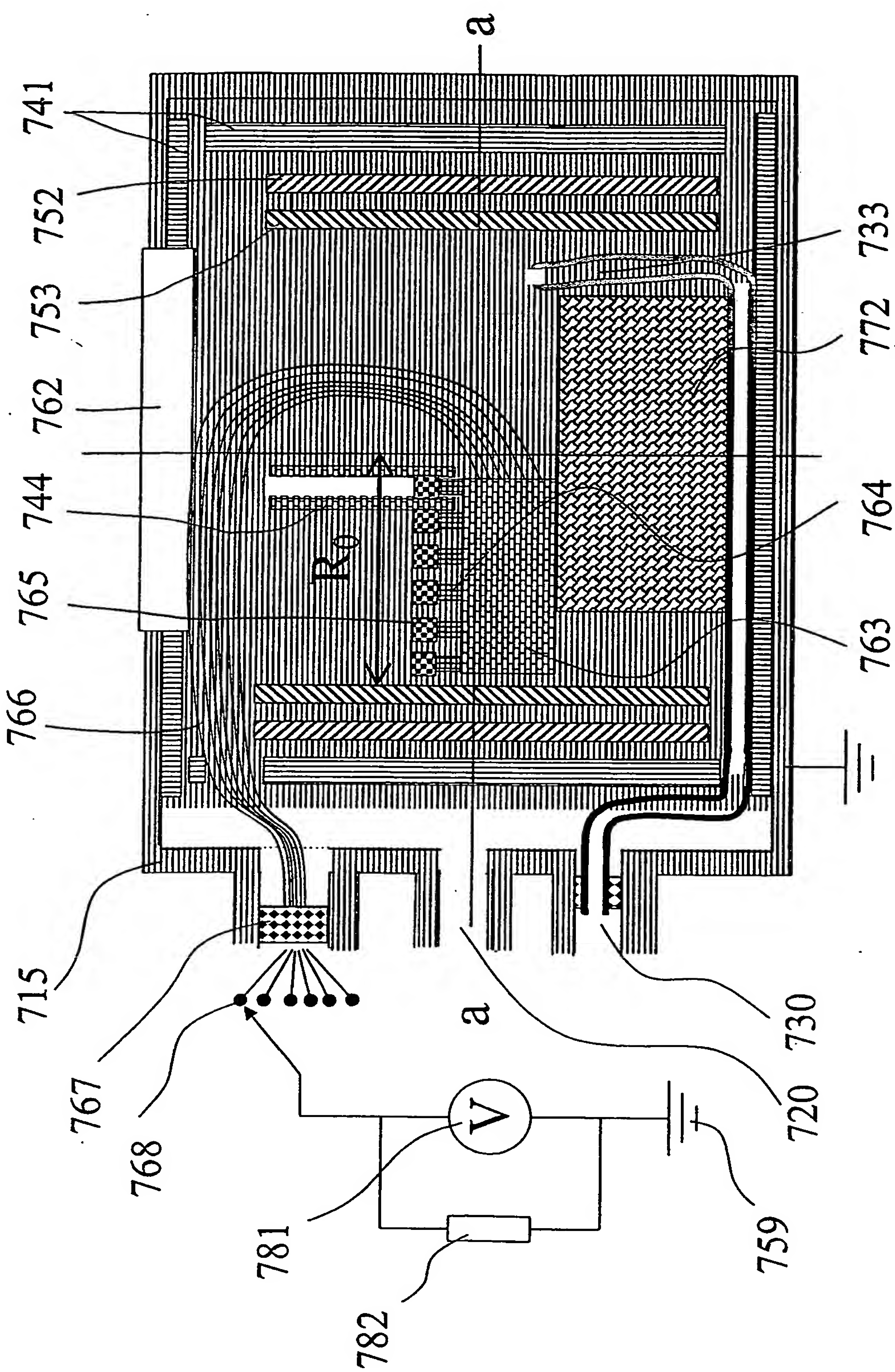


Fig. 7a


a
741
752
753
762
744
765
766
715
767
768
781
782
759
720
730
763
764
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733
R_0
V

Fig. 7b

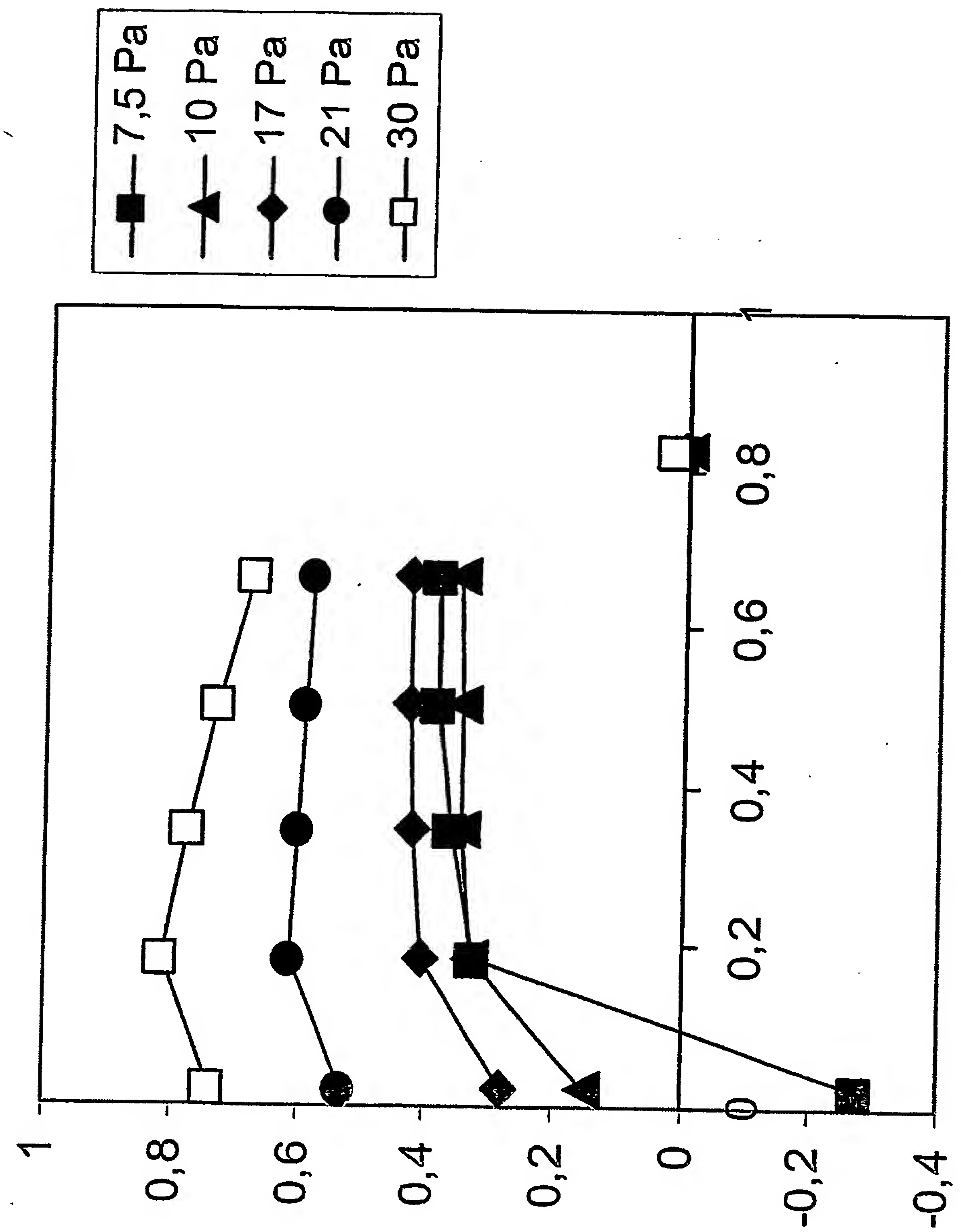

Fig. 8a

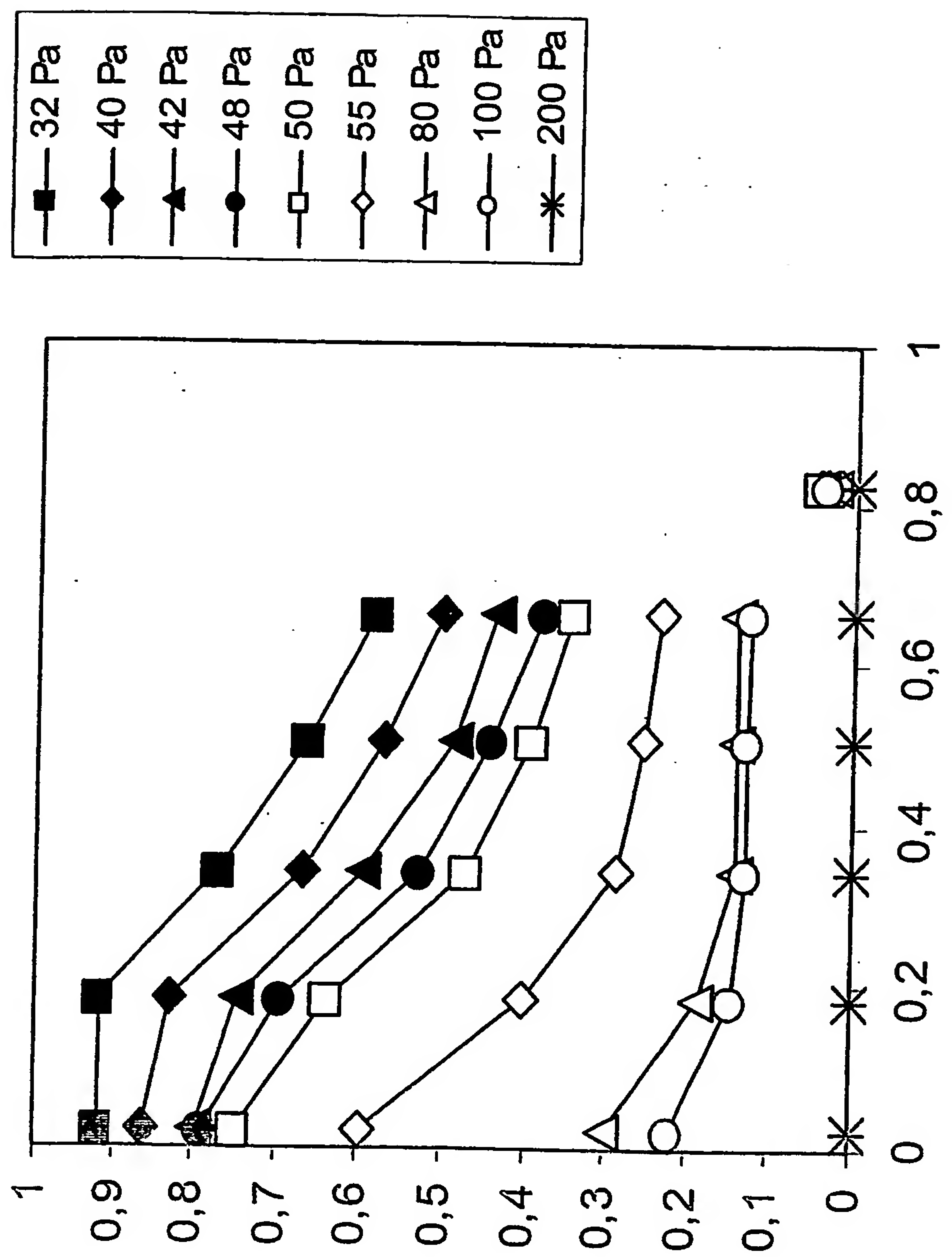
32 Pa
40 Pa
42 Pa
48 Pa
50 Pa
55 Pa
80 Pa
100 Pa
200 Pa
0
0,2
0,4
0,6
0,8
1
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1

Fig. 8b

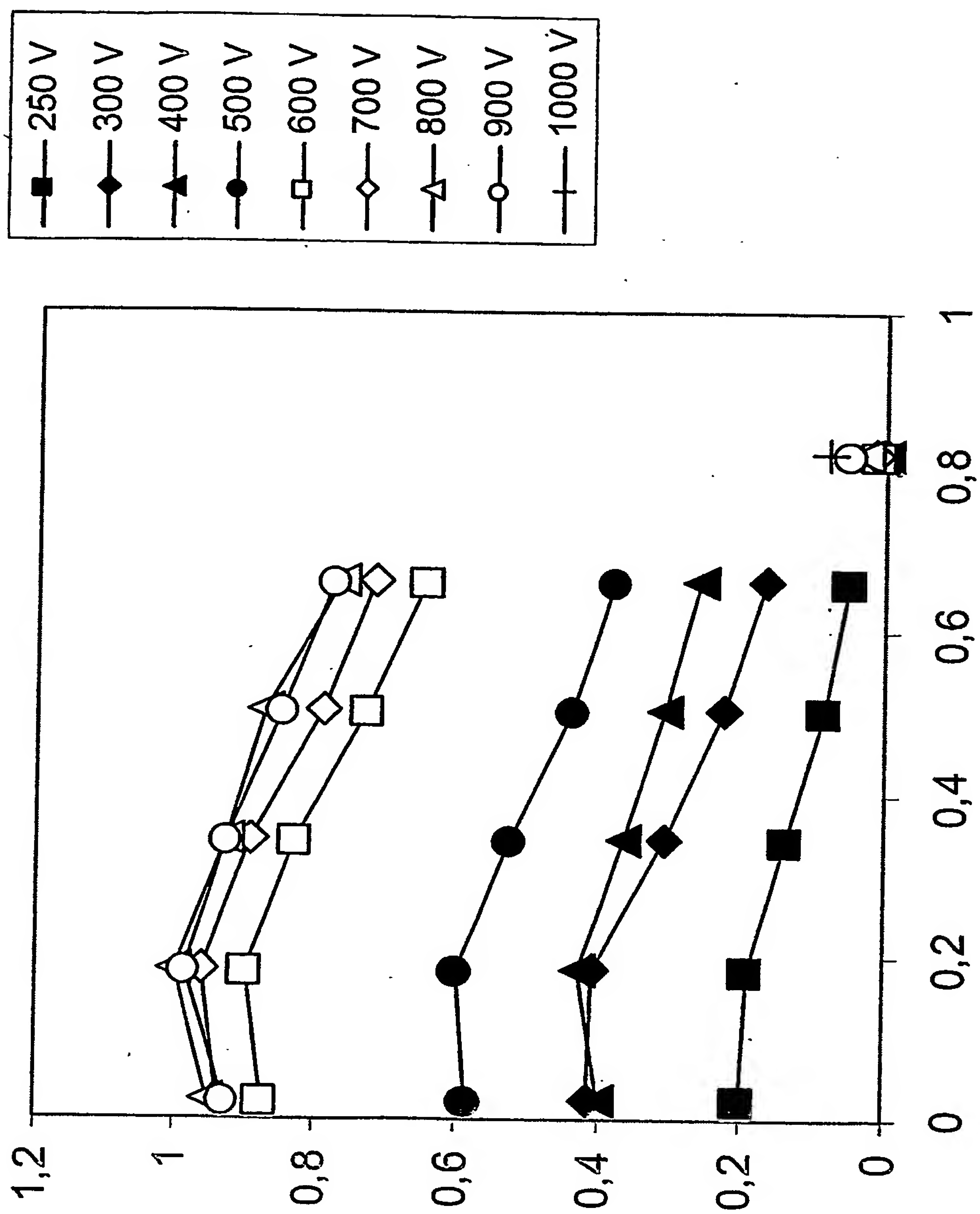
250 V
300 V
400 V
500 V
600 V
700 V
800 V
900 V
1000 V
0
0,2
0,4
0,6
0,8
1
1,2
0
0,2
0,4
0,6
0,8
1

Fig. 9